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CHEMICAL PROPERTIES OF THE FULLERENES

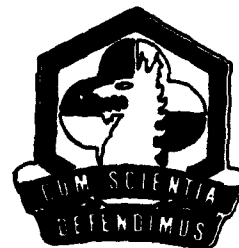
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13. ABSTRACT (Maximum 200 words) The UV-visible absorption spectra of pure C ₆₀ , C ₇₀ , and C ₆₀ O dissolved in toluene were used to perform multicomponent analysis of graphitic soot extracts and to assess the purity of fullerene samples. Diffuse-reflectance FTIR spectroscopy of 1-2 mg solid C ₆₀ and C ₇₀ samples was used to determine the fraction of hydrocarbon impurities at the level of 0.01 atom fraction H. Vacuum sublimation is the only way to produce C ₆₀ and C ₇₀ samples free of hydrocarbon impurities. The solubility of C ₆₀ and C ₇₀ in toluene was measured as a function of temperature for 25 °C < T < 80 °C, and for C ₆₀ in CS ₂ for 25 < T < 45 °C. At 30 °C, C ₆₀ is three times as soluble as C ₇₀ , but both solubilities decrease with increasing temperature. This unusual temperature dependence, exhibited by virtually no other organic solids in organic solvents, is attributed to the formation of solvated fullerene solids. The heat of combustion of C ₆₀ (cr) was determined with the NIST adiabatic bomb calorimeter, and used to determine the enthalpy of formation of C ₆₀ , 2193 ± 9.6 kJ/mol. The average strength of the carbon-carbon bonds in C ₆₀ is 453 kJ/mole. The absorption spectrum of C ₆₀ gas in equilibrium with the solid was recorded between 500 and 680 °C. From the slope of the ln(P _{eq}) vs 1/T plot, an enthalpy of sublimation for C ₆₀ of 159 kJ/mol was determined.				
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11. SUPPLEMENTARY NOTES (Continued)

***When this study was conducted, ERDEC was known as the U.S. Army Chemical Research, Development and Engineering Center, and the Contracting Officer's Representative was assigned to the Research Directorate.**

PREFACE

The work described in this report was authorized under Contract No. DAALO3-91-C-0034, Delivery Order No. 477. This work was started in June 1992 and completed in December 1992.

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I. Introduction

The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) sponsored this Short-Term Analytical Services contract with Dr. Smith and with his research group at Drexel University's Chemistry Department in order to investigate the chemical and physical properties of fullerenes¹, a new form of elemental carbon. Fullerenes have potential application as novel sorbent materials to enhance the adsorption capabilities for detoxification of highly volatile chemical warfare vapors. Of interest is the ease with which fullerenes form strong intermolecular complexes and covalently bonded adducts with other compounds, since this chemical reactivity determines the usefulness of fullerenes as sorbents. At present, not enough is known about the chemical and physical properties of fullerenes to determine their usefulness for this application. The spectroscopic and thermodynamic properties determined in this STAS contract will be helpful in assessing the relative reactivity and stability of fullerenes with respect to other forms of carbon.

II. The Proposed Work (from the rfp)

(1) Measure and report the solubility of C₆₀ and C₇₀ in benzene, toluene, CS₂, and hexane at 25°C and in 10 °C increments to 65 °C. (At the beginning of this contract, no thermodynamic information had been published on the solubility and heats of solution of any of the fullerenes in any solvent.) The temperature dependence of the solubility will be obtained by UV/visible spectrophotometry in a temperature-regulated absorption cell. An analysis of this temperature dependence will give the heats of solution of C₆₀ and C₇₀ in these solvents. Using standard thermodynamic relationships for two-component systems [C₆₀ - solvent], we shall estimate the melting point of pure C₆₀ and C₇₀, as well as the enthalpy of formation of C₆₀ and C₇₀ in these solvents

(2) Determine the heat of combustion of high-purity (a level of not greater than 0.1% of hydrocarbon impurities) C₇₀ by employing calorimetry and calculate the heat of formation of the solid C₇₀. Samples will be characterized by one or more of the following methods: diffuse reflectance FT-IR, FT nuclear magnetic resonance, and mass spectrometry.

¹ *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*; Hammond, G. S., Kuck, V.S., Eds, ACS Symposium Series 481, 1992

(3) Measure and report the vapor phase UV/visible absorption spectrum of C₆₀ and C₇₀. From the measured absorbance and a calculated relationship between solution-phase and gas-phase molar absorptivities, we will calculate the vapor pressure of C₆₀ in equilibrium with its solid phase at temperatures between 500 and 700 °C. We will plot $\ln(P_{\text{vapor}})$ versus $1/T$ (absolute temperature) to obtain the heat of sublimation of C₆₀.

III. Preparation and Characterization of Highly Pure Fullerene Samples

Fullerene Sample Preparation

The measurements described above require pure, well characterized samples of C₆₀ and C₇₀. For some time we have been using neutral alumina column chromatography for separating and purifying fullerenes from graphitic soot extract, following published methods². C₆₀ with less than 0.1% C₇₀ was obtained from the extract by preparative chromatography on neutral alumina and characterized by HPLC, FT-IR, and multicomponent UV-visible absorption. We have also employed the separation method of Tour et al³, using Norit A decolorizing carbon as the stationary phase and pure toluene as the mobile phase. However, we find the Tour method to be unsatisfactory for producing C₇₀, since all fullerenes other than C₆₀ remain adsorbed on the column even after extensive elution and must be removed by Soxhlet extraction. The chromatography of fullerenes on carbon substrates needs to be investigated further, since these substrates appear to be very promising stationary phases.

Characterization of fullerene sample purity

For some time we have been accumulating evidence (from FT-IR spectroscopy, analytical HPLC, proton nmr, and thermal gravimetric analysis) that these C₆₀ samples contain trace quantities of hydrocarbon impurities not removed by chromatography. These impurities are not the

²Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A., Science 1991, 252, 548

³ Scrivens, W. A.; Bedworth, P. V.; Tour, J. M., J. Am. Chem. Soc. 1992, 114, 7919

solvents used in extraction and chromatography (toluene and hexane), but heavier, possibly polynuclear aromatic hydrocarbons which appear to be synthesized during the production of the graphitic soot itself. This observation is supported by Guiochon and coworkers⁴, who developed a preparative chromatographic method using a C-18 column and a hexane mobile phase which effectively removes these hydrocarbon impurities. Hanna and Wilson⁵ have used cross-polarization ¹H-¹³C magnetic resonance techniques to characterize the toluene and aliphatic impurities in crude fullerene extract and their removal upon chromatography. Because the availability of fullerene samples free of hydrocarbons is essential in accomplishing our original thermodynamic measurement objectives, we have spent much time developing methods for assessing low levels of hydrocarbon impurities. We are presently investigating the purchase of a preparative C-18 column so that we can do this separation at Drexel.

UV-visible studies of fullerene-containing solutions

The molar absorptivities $\epsilon[\lambda]$ of C₆₀, C₇₀, and C₆₀O in toluene ($300 < \lambda < 800$ nm) and of C₆₀ in CS₂ ($390 < \lambda < 800$ nm) were determined by measuring absorbances of standard solutions ($0.3 - 3.0 \times 10^{-4}$ M) on a Hewlett-Packard -8451 diode array spectrophotometer. These molar absorptivity spectra, shown in Figures 1-2, agree within 10% with molar absorptivities of Wudl, Diederich et al at selected wavelengths⁶. The molar absorptivities at 338 and 384 nm⁷ for C₆₀ and C₇₀ in toluene were used in a two-component Lambert-Beer analysis to yield concentrations of C₆₀ and C₇₀ in the solution of extract from measured absorbances. The results were $[C_{60}] = 2.6 \times 10^{-3}$ and $[C_{70}] = 8.4 \times 10^{-4}$ M, a 76%/24% ratio of C₆₀/C₇₀ as expected in extract.

Multilinear regression methods were also used to perform quantitative spectrophotometric analysis of solutions containing C₆₀ and C₇₀⁸. The Lambert-Beer law for a 2-component mixture can be written as

$$A = b \epsilon c \quad [1]$$

where A is an m-component vector containing solution absorbances measured at m equally spaced wavelengths (obtained from the diode array spectrophotometer), ϵ is an m by 2 matrix containing molar absorptivities

⁴Diack, M.; Hettich, R. L.; Compton, R. N.; Guiochon, G., *Anal. Chem.* 1992, 64, 2143

⁵Hanna, J.V.; Wilson, M. A., *J. Phys. Chem.* 1992, 96, 6518

⁶P. M. Allemand, A Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Am. Chem. Soc.* 1991, 113, 1050, ref 3.

⁷For C₆₀, $\epsilon[338] = 51,000$, $\epsilon[384] = 7,860$; for C₇₀, $\epsilon[338] = 27,100$, $\epsilon[384] = 26,400$, all in units of M⁻¹cm⁻¹

⁸O'Haver, T. C., *Chemometrics and Intelligent Lab Systems* 1989, 6, 95

of the two components, c is the two-component concentration vector, and b is the (scalar) path length. The least-squares solution for the concentration vector is then

$$c = b^{-1} [\epsilon' \epsilon]^{-1} \epsilon' A \quad [2]$$

where ϵ' is the transpose of ϵ and $[\]^{-1}$ represents the inverse. The necessary matrix computations were performed using the Matlab software package⁹ on a Macintosh IICx. The residual spectrum $A - b \epsilon c$, with c determined from Eq. [2], is a sensitive probe of other absorbing impurities such as higher fullerenes. From these analyses, the mole fraction of C_{70} in all of the C_{60} samples used for solubility measurements was < 0.01 . The mole fraction of C_{60} in the C_{70} sample was determined to be < 0.03 .

FTIR studies of hydrocarbon impurities in C_{60}

The hydrogen-containing impurity content of C_{60} samples was determined by Fourier-transform infrared spectroscopy in the diffuse reflectance mode¹⁰. A 1 mg sample of C_{60} was ground with 15 mg KBr, and spectra with 2 cm^{-1} resolution were recorded with a Perkin-Elmer 1610 FT-IR (400 scans). Figure 3 shows spectra of several C_{60} samples. In addition to the four prominent vibrational fundamentals at 528, 578, 1183, and 1429 cm^{-1} , about 70 other much weaker bands are evident both in our spectra and in those of Chase et al.¹¹. These as yet unassigned bands, distributed between 600 and 2950 cm^{-1} , are probably due to combination bands built from the four observed IR fundamentals and the 42 other modes expected for C_{60} ¹². They are not due to impurities because they occur with the same relative intensities in every C_{60} spectrum we record, regardless of sample preparation. In the $2800\text{--}3100 \text{ cm}^{-1}$ region, however, bands which can be assigned¹³ to the carbon-hydrogen stretching frequencies of aliphatic and aromatic hydrocarbons appear, and their intensity relative to the C_{60} bands is a good measure of hydrocarbon impurity in fullerenes.

We define an intensity ratio $R = A(2760 \text{ cm}^{-1} \text{ to } 3100 \text{ cm}^{-1}) / (A(2620 \text{ cm}^{-1} \text{ to } 2760 \text{ cm}^{-1}))$, where the A's are integrated reflectance intensities between the given wavenumber limits. The spectral range of the denominator includes only C_{60} combination bands, with peaks at 2676 and 2737 cm^{-1} .

⁹ Matlab, by The Mathworks, Inc., Natick, MA 01760-1415

¹⁰ Griffiths, P. R.; deHaseth, J. A., *Fourier Transform Infrared Spectrometry*, 1986, Vol 83 in *Chemical Analysis*, ed P. J. Elving and J. D. Winefordner, Wiley-Interscience, pp 194ff

¹¹ Chase, B.; Herron, N.; Holler, E., *J. Phys. Chem.* **1992**, *42*, 4262, Fig. 2

¹² Negri, F.; Orlandi, G.; and Zerbetto, F., *Chem. Phys. Lett.* **1988**, *144*, 31

¹³ Lin-Vien, D.; Colthup, N. B.; Fatley, W. G.; Grasselli, J. G., **1991**, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Chaps 2 and 17

The range of the numerator includes both aromatic C-H stretches and aliphatic -CH₃ and -CH₂ stretches. Difference spectra of samples with and without hydrogen show peaks corresponding to methylene stretching vibrations (2848 cm⁻¹ and 2919 cm⁻¹) indicating the presence of aliphatic hydrocarbon impurities. The ratio R varies from ca. 1.7 for a well purified, sublimed C₆₀ sample to ca. 60 for a needle-like C₆₀ sample crystallized slowly from toluene.

Diffuse reflectance FTIR spectra of samples with known atom fractions of hydrogen from neutron activation analysis and from Rutherford backscattering¹⁴ were used to determine the hydrogen content of the samples under study here. The results are shown in Table 1.

Differential scanning calorimetry (DSC) studies of the first-order phase transition in C₆₀ at 260 K¹⁵ show that the phase transition temperature and the width of the DSC peak are very sensitive to sample purity. DSC measurements of most of the samples in Table 1, done by A. R. McGhie of the University of Pennsylvania, show that the sublimed samples have the sharpest DSC peaks and the highest transition temperature. These are also the samples which show the lowest C-H stretch/C₆₀ band FT-IR intensity ratio R.

Hydrocarbon impurities in C₇₀

FT-IR specoscopy in combination with x-ray diffraction is also useful in characterizing hydrocarbon impurities in C₇₀¹⁶. For the first set of diffraction measurements, C₇₀ samples were used which had been dried at 200°C for two hours under vacuum to remove residual hexane, the last solvent with which the sample had been washed. Evidence that this process did not remove toluene (another solvent used in the chromatographic separation) was obtained from a diffuse-reflectance infrared spectrum of the sample, shown in Figure 4 A. Previously identified¹⁷ infrared bands of C₇₀ were observed¹⁸, but two additional bands at 694 cm⁻¹ and 724 cm⁻¹ can be attributed to the two strongest

¹⁴C. Kniaz and J. E. Fischer, Dept. of Materials Science, University of Pennsylvania, private communication

¹⁵Yannoni, C.S.; Wendi, H. R.; Siemens, R. L.; Salem, J. R.; Nguyen, D.

Lyria, J.; Johnson, R. D.; Hoinkis, M.; de Vries, M. S.; Crowder, M. S.; Brown, C. A., Intl. Conf. on Synthetic Metals, Goteborg, Sweden, Aug 12-16, 1992, in press

¹⁶Vaughan, G. B. M.; Heiney, P. A.; Fischer, J. E.; Luzzi, D. E.; Ricketts-Foot, D. A.; McGhie, A. R.; Hui, Y. W.; Smith, A. L.; Cox, D. E.; Romanow, W. J.; Allen, B. H.; Coustel, N.; McCauley, J. P.; Smith III, A. B., *Science* 1991, 254, 1350

¹⁷Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J.; Golden, W. G.; Seki, H.; Brown, C. A.; de Vries, M. S., *Chem. Phys. Lett* 1991, 179, 181

¹⁸ bands at 504, 534, 564, 578, 642, 674, 794, 1134, 1430 cm⁻¹ (± 2 cm⁻¹)

infrared absorptions of toluene¹⁹, corresponding to C-H out-of-plane bending modes. Additional bands between 1416 and 1566 cm^{-1} are less easily assigned, but are consistent with C=C stretching modes of the benzene ring in the toluene spectrum³. The methyl group bending modes observed in the 1350-1400 cm^{-1} spectrum of hexane²⁰ are absent.

The final step of sample preparation was changed. The C₇₀ sample containing residual hexane was heated to 550°C under vacuum for 12 hours in a horizontal quartz tube with a cooled end. The sublimed film formed on the cool end of the tube was then scraped off; its FT-IR spectrum is shown in Figure 4b. Note the absence of bands due to toluene.

We conclude that vacuum sublimation is essential in preparing highly pure C₆₀ and C₇₀ samples suitable for thermodynamic measurements. It is not surprising that aromatic solvents are hard to remove from fullerenes. Each carbon in C₆₀ has an unshared p-orbital normal to the surface of the icosahedron, and these orbitals should overlap with the pi-orbitals of the benzene ring to form a van der Waals pi complex. In addition, there are large voids in the C₆₀ crystal structure due to the octahedral and tetrahedral holes in the fcc structure, and these voids could hold solvent if slightly expanded.

IV. Temperature Dependence of The Solubility of C₆₀ and C₇₀ in Toluene and Carbon Disulfide (manuscript in preparation)

Abstract

During the past year we have measured the solubility of C₆₀ and C₇₀ in toluene from 25 °C to 80°C and of C₆₀ in CS₂ from 25 to 45 °C. The method has been to measure the concentration of saturated solutions of the fullerene using UV/visible absorption spectrophotometry. The most remarkable feature of these data is that as the temperature increases, the solubility of both C₆₀ and C₇₀ decrease. This is highly unusual for organic compounds in organic solvents - so much so, in fact, that despite my have done several literature searches, consulted databases of organic solubilities and current comprehensive literature²¹, and asked experts on organic

¹⁹Sadtler Research Labs, Standard IR Spectra, #419, Philadelphia, PA 1962

²⁰op. cit, #678

²¹Grant, D. W. J.; Higuchi, T., "Solubility Behavior of Organic Compounds", 1990, Vol XXI of Techniques of Chemistry, Wiley-Interscience

solubility²², I have not been able to find any other organic compound which exhibits a negative temperature dependence of the solubility.

Introduction

One of the classical ways to study intermolecular interactions between two substances is to determine their mutual solubility ^{20, 23}. The notion of ideal and regular solutions evolved from thermodynamic and statistical mechanical investigations of solubility. In addition, the solubility of chemical substances plays a key role in their isolation and purification and the control of their chemical reactivity. Experimental study of the fullerenes²⁴ grew explosively after it was discovered by Krätschmer, Huffman, et al²⁵ that a component of the graphitic soot produced by electric arcs could be dissolved in benzene. Yet, aside from footnotes in the burgeoning fullerene research literature, the first quantitative study of the solubility of C₆₀ in various organic solvents was only recently published. Mathews et al²⁶ measured solubilities of C₆₀ in fifteen organic solvents at 303 K, and they explain the large variation (a factor of $\sim 10^3$) in terms of Hildebrand's theory of regular solutions. They suggest that C₆₀ has a solubility parameter of ca. 18.5, closely matching that of toluene and benzene. Ruoff et al²⁷ report the temperature dependence of C₆₀ solubility in hexane, toluene, and CS₂ over the temperature range 195 K to the normal boiling point of each solvent. The solubility/temperature curve displays a maximum at ca. 280 K. We have chosen toluene and CS₂ as solvents in this study because of their importance in both the extraction of the fullerenes from soot and their subsequent chromatographic purification.

Experimental method and results

For the initial studies²⁸ (February - April 1992), C₆₀ and C₇₀ were separated and purified from the extract of graphitic soot provided by W. A. Romanow of the University of Pennsylvania. Preparative

²²telephone conversation with Dr. D. W. J. Grant, February 16, 1993

²³Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. , 1970 , Regular and Related Solutions, Van Nostrand Reinhold

²⁴Kroto, H. W. ; Allaf ,A. W. ; Balm, S. P., Chem. Rev. 1991, 91 , 1213

²⁵W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature 1990 , 347 , 354

²⁶Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Vasudeva Rao, P. R.; Mathews, C. K., J. Org. Chem. 1992, 57, 6077

²⁷Ruoff, R. S.; Malhotra, R.; Huestis, D. L.; Tse, D. S.; Lorents, D. C., "The Unusual Solubility Behavior of C₆₀", Nature 1993, in press

²⁸A. L. Smith, Y. W. Hui, and D. Li, presentation at 186th Electrochemical Society meeting, St. Louis, MO, April 1992

chromatography as previous described was performed using neutral alumina (Fisher, Brockman Activity 1), and reagent grade hexanes and toluene. Solvents were removed with a rotary evaporator, and samples were dried in 1×10^{-4} torr vacuum at 200 °C for 6 hours and then characterized by diffuse reflectance FTIR and HPLC (Regis phenylglycine column with hexane as mobile phase). For later C₆₀ solubility measurements in toluene and in CS₂, a sample obtained from Texas Fullerenes was used without further purification. The C₆₀ and C₇₀ content of the original extract and of the separated solutions was determined by quantitative UV/visible absorption with a HP 8451 diode array spectrophotometer, as described above.

For our first measurements on C₆₀ in toluene (February-March, 1992) saturated solutions were prepared in a 1.0 cm path length quartz cell held in a stirred, thermostatted cell holder (± 0.1 °C) at temperatures of between 25 and 75 °C (measured with a calibrated thermocouple placed in the cell itself). After the stirrer was turned off, the solution was allowed to settle for 1-2 hours and the absorbance measured. These measurements showed clearly that the solubility of C₆₀ decreased with increasing temperature, but the spectra also exhibited positive baseline shifts of up to 1.2 a.u. in the near infrared, which we attribute to optical scattering of undissolved, suspended C₆₀ (the density of fullerenes is < 2 g/cm³, so material settles out of solution very slowly). Absorbances were too large to make good concentration measurements, so we shifted to 1.0 and 2.0 mm path length cells. The data sets of 4/21/92 and 6/16/92, taken after allowing shaken solutions to equilibrate and settle for an hour, showed residual absorption at 750 nm due to optical scattering of less than 5% of the absorbance at 590 nm. Absorbances between 500 and 600 nm (0.2 -0.8 a.u.) were corrected for this residual baseline, and C₆₀ concentrations were then determined at 50 wavelengths and averaged to determine the concentration of the saturated solution. The data are plotted in Figure 5.

For the data sets of 7/20/92 and 7/24/92, stirred, saturated solutions were allowed to settle for an hour, then 30-40 μ l was withdrawn into a glass syringe. A syringe filter was added between the syringe and the needle to remove suspended crystallites, and the solution was then expelled into the 1.0 mm path length cuvette and the cuvette was quickly capped. Even though the temperature of the saturated solution may well have dropped in the process, the inverse dependence of solubility on temperature assured that no solid precipitated out. The data (Figure 5) show solubilities from 10-30% lower than earlier (or later) measurements, which we attribute to slight absorption of C₆₀ on the filter material.

The final data sets of Figure 5 (11/16 and 11/1792) were obtained from the Texas Fullerenes C₆₀ sample, measured in a sealed 2.0 mm cell allowed to equilibrate for an hour.

The two data sets for C₇₀ in toluene (Figure 6) were taken on 4/20/92 and 4/22/92, and agree well with one another. The two data sets for C₆₀ in CS₂ (Figure 7) were taken in December 1992; particular care was taken to seal the 2.0 mm cuvette with Teflon tape so as to prevent CS₂ from evaporating and forming a supersaturated solution.

Discussion

Ruoff et al have recently reported that the solubility of C₆₀ in toluene, CS₂, and hexane all shows negative temperature dependence for T > 280 K. From thermodynamics it can be shown that a negative temperature dependence of solubility implies an exothermic heat of solution, ΔH^{soln} . If we assume that the equilibrium

$$C_{60}(s, T) = C_{60}(\text{satd soln}, x_{C_{60}}, T), \quad [1]$$

($x_{C_{60}}$ = mole fraction of C₆₀ in the saturated solution)

is established, from the thermodynamics of solid solubility²⁹, the enthalpy of solution of C₆₀ is given by

$$\Delta H^{\text{soln}} = H_{C_{60}} - H_{C_{60}}^s = -R \left(\frac{\partial \ln x_{C_{60}}}{\partial (1/T)} \right)_{\text{sat}} \quad [2]$$

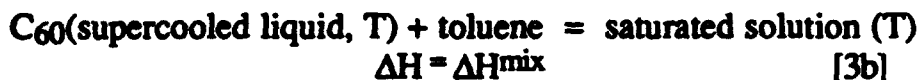
The resulting enthalpies of solution vary from -10.7 kJ/mole to -18.1 kJ/mole for the various data sets of Figure 5, with a mean value of -13.6 ± 2.5 kJ/mole. This is in reasonable agreement with Ruoff et al's value of -11 ± 2 kJ/mole.

The negative heat of solution for the system C₆₀/toluene is hard to understand. The theory of regular solutions^{20, 22}, based on modifications of the theory of ideal solutions, is quite successful in correlating solubilities of organic compounds in organic solvents. For an ideal solution of two liquids, the enthalpy of mixing ΔH^{mix} is zero; for an ideal solution of a solid and a liquid, the enthalpy of solution is positive and equal to the enthalpy of fusion of the solid. Regular solutions show positive deviations from the ideal solution theory heats of solution. Polynuclear aromatic

²⁹Ref 22, eqn 2.57, page 24

hydrocarbons form almost ideal solutions with benzene³⁰, and their solubilities increase with temperature, as shown in Figure 8.

The dissolution of solid C₆₀ in toluene may be described as a two-step process:



The enthalpy change for 3a is approximately the heat of fusion of C₆₀ if one ignores the heat capacity differences between solid and supercooled liquid. Thus,

$$\Delta H^{\text{soln}} = \Delta H^{\text{fus}} + \Delta H^{\text{mix}}. \quad [4]$$

Although ΔH^{fus} is not known (since the melting point T_m of the solid has not been observed and must be greater than 900 °C³¹), we can estimate it as follows. We assume that at the melting point, C₆₀ molecules are freely rotating in the solid phase, as they are known to be at room temperature. Thus, the only contribution to the entropy of fusion $\Delta S^{\text{fus}} = \Delta H^{\text{fus}} / T_m$ of C₆₀ comes from "positional melting". It is known that this contribution to ΔS^{fus} for rigid spherical molecules is about 10.5 J/mole³². Taking $T_m = 1173$ K, we obtain $\Delta H^{\text{fus}} \approx 12$ kJ/mole. The enthalpy of sublimation of C₆₀ is known to be 39 kJ/mole³³, so $\Delta H^{\text{fus}}/\Delta H^{\text{subl}} \approx 0.3$. This is a reasonable result, since other rigid, nearly spherical organic molecules have similar ratios³⁴. Since the observed heat of solution of C₆₀ in toluene, assuming the equilibrium in Eq. 1, is -13.6 kJ/mole, from Eq. [4] we obtain $\Delta H^{\text{mix}} \approx -25.6$ kJ/mole.

We submit that such a large, negative heat of mixing is unrealistic. It implies very large negative departures from Raoult's law and solution ideality, yet there seems to be no plausible microscopic reason why so much energy is released when forming a solution between molecules whose

³⁰D. S. Mishra and S. H. Yalkowski, *Ind. Eng. Chem. Res.* 1990, 29, 2278

³¹X-ray powder diffraction patterns of the solid are still observed at 900 °C (G. Vaughan and P. Heiney, private correspondence)

³²Yalkowski, S. H., *Ind. Eng. Chem. Fundam.* 1979, 18, 108

³³Mathews, C. K.; Baba, M. Sai; Lakshmi Narasimhan, T. S.; Balasubramanian, R.; Sivaraman, N.; Srinivasan, T. G.; Vasudeva Rao, P. R., *J. Phys. Chem.* 1992, 96, 3566

³⁴For example, the ratio for adamantane is 0.22. (C. Kniaz, U. Pennsylvania, private communication)

electronic structure is similar (aromatic rings and pi electron density on the "surface" of each). Admittedly, the low-density, fcc structure³⁵ of C₆₀ in the solid does not permit close contact between solute molecules, whereas the solute-solvent contact in the solution is more intimate and thus the van der Waals interactions are probably stronger. Yet it is very hard to believe that such effects could account for a heat of mixing of two liquids which is almost as large as the heat of sublimation of one of the corresponding solids.

We must thus seek another explanation for the negative temperature dependence of the solubility of C₆₀ in toluene. Ruoff et al have proposed that the primary contribution to the negative temperature dependence is the formation of a solid solution of C₆₀ and solvent, with increasing mole fraction of solvent at increasing temperatures. In equation [1] we assumed that the solid phase was pure C₆₀, yet evidence from crystallography and from vibrational spectroscopy shows that C₆₀ indeed forms stable inclusion compounds with pentane³⁶ and a number of other organic solvents³⁷. Thus, the formation of toluene inclusion compounds is likely.

As Grant and Higuchi prove, "A rule applying to solubility is that solid solvates are always less soluble in the solvent forming the solvate than is the original solid."³⁸ When C₆₀ precipitates from a saturated solution in toluene, the resulting solid may not be a pure phase but a mixture of pure C₆₀ and of toluene inclusion compounds, with ill-defined stoichiometry. This mixed phase solid will have a lower apparent "equilibrium solubility" than would pure C₆₀. The rate of formation of solvated solid phase probably depends upon the temperature, the degree of supersaturation, and the availability of nucleating crystallites. Thus, the longer we wait for equilibrium to occur, the more the solid material in equilibrium with the solvent changes its composition to solvated solid. This makes the determination of true equilibrium solubilities of unsolvated solid fullerenes more difficult. The non-reproducibility shown in Figure 5 for the "equilibrium solubility" of C₆₀ in toluene at various temperatures may well be due to the formation of solid phases of variable solvent composition. We are investigating this possibility at present, using FTIR spectroscopy to determine the percentage of solvent trapped in the C₆₀ crystal. Preliminary studies of the solid precipitating from saturated toluene at 50

³⁵Fischer, J. E.; Heiney, P. A.; Smith, A. B. III, *Accts Chem. Res.* 1992, 25, 112

³⁶Pekker, S.; Faigel, G.; Fodor-Csorba, K.; Granasy, L.; Jakab, E.; Tegze, M., *SOLID State Comm.* 1992, 83, 423

³⁷Kameras, K.; Hadjiev, V. G.; Thomsen, C.; Pekker, S.; Fodor-Czorba, K.; Faigel, G.; Tegze, M., *Intl. Conf. on Synthetic Metals*, Goteborg, Sweden, Aug 12-16, 1992, in press

³⁸Ref. 20, page 38

*C indicates that at early times the solid includes a good deal of toluene, whereas at later times the solid is pure C₆₀. Without a direct measurement of the percentage of solvent included in the precipitated solid in a solubility experiment, the "equilibrium" solubilities reported here or elsewhere cannot be accepted as the true thermodynamic solubilities.

Figure 6 implies that the heat of solution of C₇₀ in toluene is also negative over the temperature range studied, and a fit of the data to $\ln[C_{70}]$ vs $1/T$ gives a heat of solution of -5.2 ± 0.7 kJ/mole. Since C₇₀ shows two rotational disordering transition at 276 K and 337 K¹⁵, Ruoff et al's observation that the maximum of the solubility vs temperature curve (280 K) for C₆₀ is correlated with the occurrence of an order-disorder phase transition (260 K) does not hold in C₇₀.

A case can be made from the data in Figure 7 that the solubility of C₆₀ in CS₂ is independent of temperature, although the scatter is rather large. This disagrees with the results of Ruoff et al, who found similar heats of solution of C₆₀ in toluene and CS₂. Further work is needed to resolve this discrepancy.

In separating and purifying the fullerenes, we have noticed gradations of color of the deposit as the solvent is removed from the extract of the raw soot, suggesting that C₆₀ and C₇₀ are precipitating out under different conditions. A more systematic study of selective precipitation of C₆₀ within a Soxhlet extractor has been reported by Coustel et al³⁹. As the toluene solvent from soot extract with a 4:1 ratio of C₆₀:C₇₀ is slowly allowed to evaporate within a Soxhlet extractor, 98% pure C₆₀ selectively precipitates in the solvent flask. This observation can be explained as follows. The extraction temperature T_1 in the thimble of a Soxhlet extractor is undoubtedly lower than the boiling point of the solvent, T_2 , since no heat is applied to the extractor thimble. Thus, the solubility of fullerenes in the thimble exceeds the solubility in the solvent flask. Even though C₆₀ is several times more soluble than C₇₀, as the extract at T_1 mixes with the solution at T_2 the solution becomes saturated first with respect to C₆₀, and C₆₀ precipitates.

Clearly there is much to learn about the solute-solvent intermolecular interactions in fullerene/organic solvent systems which exhibit such unusual temperature dependencies. The fact that the solubilities of C₆₀ and C₇₀ are different and also show different temperature dependencies could form the

³⁹ Coustel, N.; Bernier, P.; Aznar, R.; Zamed, A.; Lambert, J.-M.; Lyard, P. J. Chem. Soc. Chem. Comm. 1992, 19, 1402

basis for a separation process which completely avoids chromatography and thus would be more amenable to large-scale industrial production.

The fact that van der Waals interactions between typical solvents and fullerenes are so strong has definite implications for the eventual use of fullerenes as adsorbents. By further understanding why these interactions are so large, we should put on a better basis the intermolecular interactions between carbonaceous solids and volatile materials, thus helping to understand why standard carbon materials are good adsorbents. It will be very important to characterize these strong interactions better by studying further the solubilities of fullerenes in other organic solvents, including those which more closely match the organic vapors whose removal from air is of interest to the Army.

The authors would like to thank Jack Fisher and the other members of the U. Penn buckyball research group for many useful discussions.

V. Experimental Heat of Formation and Average Carbon-Carbon Bond Energy in C₆₀, Buckminsterfullerene (manuscript in preparation)

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Abstract

Using the NIST aneroid adiabatic rotating calorimeter, we have measured the energy of combustion of a pure, well characterized sample of C₆₀. The standard molar enthalpy of combustion $\Delta_c H_m^0$ is $-(25803.9 \pm 5.6)$ kJ·mol⁻¹. The derived enthalpy of formation of C₆₀(c) is (2193.3 ± 9.6) kJ·mol⁻¹, somewhat lower than reported values of this quantity. Using the enthalpy of formation of C(gas) we calculate that the average carbon-carbon bond

energy in C_{60} is 453 kJ/mol, less than in graphite but more than in diamond.

Introduction

The strengths of the covalent bonds in organic compounds are of fundamental importance in understanding their structure and reactivity. It is well known⁴⁰ that thermochemical heats of formation may be combined to compute bond strengths. In this paper we report an experimental measurement of the heat of formation of solid C_{60} , Buckminsterfullerene, and we use this number to compute the average carbon-carbon bond energy in C_{60} .

By definition, the standard heat of formation of graphite, $C(cr)$, at 298.15 K, 1 atm, is zero. When graphite is burned in oxygen,



the standard heat of combustion of graphite is equal to the standard heat of formation of carbon dioxide, $\Delta_f H_m^0[CO_2(g)]$. The heat of combustion of graphite is measured to be -393.509 kJ·mol⁻¹. Since C_{60} is less thermodynamically stable than graphite, its heat of combustion must be larger than that of graphite.

Newton and Stanton⁴¹ first reported a quantum calculation of the heat of formation of C_{60} , based on the semi-empirical MNDO method. Their result is +14.5 kcal · mol⁻¹ (per mole of C), or 3640 kJ · mol⁻¹ (per mole of C_{60}). Another MNDO study of large carbon clusters⁴² reports a value of 13 kcal · mol⁻¹ (of C), or 3260 kJ · mol⁻¹ (of C_{60}). Schulman and Disch⁴³ have used a 6-31G* SCF energy of C_{60} in combination with group equivalent methods to arrive at a value of 11.2 kcal · mol⁻¹ (of C), or 2811 kJ · mol⁻¹ (of C_{60}). These computations are all for gaseous C_{60} , but they can be corrected to the solid form by subtracting the heat of sublimation of C_{60} ^{32, 44, 45}.

Experimental Section

⁴⁰Benson, S. J. *Chem Ed* 1965, 42, 502

⁴¹Newton, M. D.; Stanton, R. E., *J. Am. Chem. Soc.* 1986, 108, 2469

⁴²Bakowies, D.; Thiel, W., *J. Ann. Chem. Soc.* 1991, 113, 3704

⁴³J. M. Schulman and R. L. Disch, *J. Chem. Soc. Chem. Comm.* 1991, 411

⁴⁴Pan, C.; Sampson, M. P.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* 1991, 95, 2944

⁴⁵Tokmakoff, A.; Haynes, D. R.; George, S. M., *Chem. Phys. Lett.* 1991, 186, 450

The soot from a graphite rod arc reactor was extracted with room temperature toluene, producing a fullerene mixture which by high-performance-liquid-chromatography on a Pirkle column contained about 75% C₆₀, 20% C₇₀, and 5% higher fullerenes. Neutral alumina column chromatography fractions, using 5% to 20% toluene in hexanes, were monitored with a diode-array UV-visible spectrophotometer to assay the fullerene composition in real time, and an early C₆₀ fraction was selected which had no contamination from C₆₀O. Solvent was removed in a rotary evaporator at 80°C, and the dried sample (finely divided brown powder) was washed three times with reagent grade hexane. The sample was redissolved in toluene, filtered to remove residual alumina, pumped to dryness in a rotary evaporator, washed with diethyl ether, then dried under vacuum (ca 1 Pa, or 10⁻³ torr) at 230 °C for 6 hours. The weight loss of the sample during drying was 3.2%. An electron-impact mass spectrum of the resulting dark brown sample showed only mass 720 and 721. The sample redissolved slowly in toluene, and its UV-visible spectrum was identical to that of other samples of >99.9% fullerene purity prepared at the University of Pennsylvania. Pirkle column hplc confirmed that the C₇₀ content was less than 0.1%.

Because of the large effect of residual hydrocarbon impurities on the apparent heat of formation of C₆₀ (0.1% of toluene by weight will increase $\Delta_f H^0_m[C_{60}(c)]$ by 1.1%), an effort was made to characterize the hydrogen content of the sample. Diffuse reflectance infrared spectroscopy of the sample (5% in KBr) showed weak C-H stretch bands in the 2900-3100 cm⁻¹ region, but no C₆₀ sample of known hydrocarbon content was used to quantify this residual hydrogenic impurity.

The NIST adiabatic bomb calorimeter was used for the heat of combustion measurements. It is a vacuum-jacketed, aneroid calorimeter with an adiabatic shield around the calorimeter. A calibrated capsule-type platinum resistance thermometer is located in the bomb wall. A constant current source was passed through the platinum resistance thermometer and a calibrated standard resistor. The resulting voltages were measured with a high precision nanovoltmeter. A more comprehensive description of the calorimeter system can be found in an earlier paper by Kirklin and Domalski.⁴⁶

The calorimeter was calibrated by a series of combustion experiments using benzoic acid, NIST SRM 39i. The calorimeter is normally calibrated for a three- or one-degree temperature rise. Since the total C₆₀ sample was

⁴⁶Kirklin, D. R.; Domalski, E. S. J. Chem. Thermodynamics 1983, 15, 941

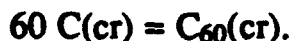
only 100 mg, the calorimeter was calibrated for only 0.5 degree temperature rise. The C_{60} analysis samples were not large enough to produce a 0.5 degree temperature rise and therefore a small pellet of benzoic acid was used as an auxiliary substance. A mass of benzoic acid was chosen to produce half of the measured energy. A standard procedure for bomb calorimetric measurements was followed for these measurements.

The results of the set of calibration measurements and the C_{60} combustion measurements are presented in Table 2. All calculations were performed using a computer program originally written by C. H. Shomate⁴⁷ and later revised by G. T. Armstrong⁴⁸ according to the methods of Hubbard, Scott, and Waddington.⁴⁹ The calculations required several auxiliary values. Thermochemical quantities for $CO_2(g)$ and $O_2(g)$ were taken from Wagman et al.⁵⁰ and CODATA.⁵¹ The molar mass of C_{60} is $720.66 \text{ g} \cdot \text{mol}^{-1}$ and is based on the 1985 Table of International Atomic Weights.⁵² The density and specific heat capacity of C_{60} were taken as $2.25 \text{ g} \cdot \text{cm}^{-3}$ and $0.397 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$, respectively. The value of the gas constant used in the calculations is $R = 8.314510 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.⁵³ The standard heat capacities used for CO_2 and O_2 were 37.11 and $29.355 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively. The $\Delta_f H_m^0$ for CO_2 is $-393.509 \text{ kJ} \cdot \text{mol}^{-1}$ and was used to convert from $\Delta_c H_m^0$ to $\Delta_f H_m^0$.

The enthalpy of combustion was determined for the following chemical reaction:



The combustion data were used to calculate the enthalpy of formation of crystalline C_{60} at 298.15 K by the following reaction:



⁴⁷(a) Shomate, C. H. U. S. Naval Ordnance Test Station Technical Report 327. August 1963, China Lake, CA. (b) Shomate, C. H. U. S. Naval Ordnance Test Station Technical Report 5052. January 1967, China Lake, CA.

⁴⁸Armstrong, G. T. Nat. Bur. Stand. Report 9803, 1968, chap. 3.

⁴⁹Hubbard, W. N.; Scott, D. W.; Waddington, G. J. Phys. Chem. 1952, 58, 152

⁵⁰Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. J. Phys. Chem. Ref. Data 1982, 11, Supplement no. 2

⁵¹CODATA recommended key values for thermodynamics 1977, CODATA Bulletin 28, April 1978

⁵²Holden, N. E.; Martin, R. L. Pure Appl. Chem. 1986, 58, 1677

⁵³CODATA 1986 recommended values of the fundamental physical constants. CODATA Newsletter 38. October 1986.

The calculated thermochemical results are presented in Table 3. The total uncertainty was calculated according to the guidelines presented by G. Olofsson⁵⁴. The assigned uncertainty is equal to twice the overall standard deviation which includes components for sample measurements, calibration measurements, and benzoic acid certification measurements⁵⁵. In addition, there are components for the auxiliary substance and estimated uncertainties of 0.01 percent each for sample impurities and systematic error. The uncertainty in the enthalpy of formation contains a component for the uncertainty in the enthalpy of formation of CO₂(g).

Results and Discussion

There have been two other experimental determinations of the enthalpy of formation of C₆₀^{56, 57}. The three sets of measurements are summarized in Table 4. Clearly there is disagreement within the stated experimental precision. We believe that this is due to inadequately characterized samples, particularly with respect to the hydrocarbon content. The work discussed in previous sections shows that it is very difficult to remove the last traces of solvent except by vacuum sublimation, and none of the three groups did this. We are working to produce the purest sample of C₆₀ and C₇₀ possible with present technology. When this becomes available, we will forward the samples to NIST for their calorimetric measurements.

In Figure 9 we present the enthalpy of formation of different allotropic forms of carbon, in kJ per mole of atoms. Our experimental result is in reasonable agreement with the calculations of Schulman and Disch. Notice that Buckminsterfullerene, C₆₀, is much less thermodynamically stable than either graphite or diamond. Of course this does not tell us how chemically stable C₆₀ is with respect to degradation into graphite (or diamond, for that matter). Only further experimental work will elucidate the chemical reactivity of this unusual all-carbon molecule.

Strengths of carbon-carbon bonds in carbon allotropes

⁵⁴Olofsson, G. *Combustion calorimetry*. 1979, Sunner, S.I. Mansson, M.: editors. Pergamon: New York, , chap. 6.

⁵⁵Churney, K. L.; Armstrong, G. T. *J. Res. Nat. Bur. Stand.* 1968, 72A, 453.

⁵⁶Beckhaus, H.-D; Ruchardt, C.; Kao, M.; Diederich, F.; Foote, C. S.. *Angew. Chem. Int. Ed. Engl.* 1992, 31, 63

⁵⁷Steele, W. V.; Chirico, R. D.; Smith, N. K.; Billups, W. E.; Elmore, P. R.; Wheeler, A. E.. *J. Phys. Chem.* 1992, 96, 4731

By using thermochemical information on the carbon allotropes themselves, it is possible to calculate and compare the strength of the carbon-carbon bond in diamond, graphite, and Buckminsterfullerene without reference to any organic compound containing hydrogen, oxygen, or other elements.

The carbon-carbon single bond.

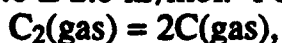
From the accepted heats of formation of diamond and gaseous atomic carbon⁵⁸, the molar enthalpy change for the atomization of diamond,



is 714.9 ± 0.5 kJ/mol. In the atomization process, two moles of C-C bonds are broken per mole of diamond atomized, so the carbon-carbon single bond strength in diamond is 357.5 ± 0.5 kJ/mol. This is lower than the accepted C-C bond strength in ethane, 376.1 ± 2.1 kJ/mol, but it is well known that varying the substituents on sp³ hybridized carbons affects the C-C bond energy by as much as 15-20 kJ/mol.

The carbon-carbon double bond.

An accurate experimental heat of formation of the gaseous carbon dimer, C₂, has recently been reported by Jackson and coworkers⁵⁹: $\Delta_f H_m^0[\text{C}_2(\text{g})] = 815.0 \pm 2.0$ kJ/mol. For the dissociation reaction



the standard enthalpy change is thus 618.3 ± 2.2 kJ/mol, which we take as the strength of a carbon-carbon double bond. This is again lower than the accepted value of the C=C bond energy in ethylene⁶⁰, 720 ± 8 kJ/mol. but well above the carbon-carbon double bond energy in C₂F₄, 319 kJ/mol⁶¹

The carbon-carbon bond in graphite

In graphite, the atoms within a sheet are bonded covalently whereas the interaction between sheets is intermolecular (Van der Waals bonding). A convenient reference state for atomization calculations is the infinite graphite sheet, whose enthalpy with respect to graphite has been calculated

⁵⁸Cox, J. D.; Wagman, D. D.; Medvedev, V. A., *CODATA Key Values for Thermodynamics*, 1989, Hemisphere Publishing Company

⁵⁹Urdahl, R. S.; Bao, Y.; Jackson, W. M., *Chem. Phys. Lett.* 1991, 178, 425

⁶⁰Value calculated using enthalpy data from Cox, J. D., and Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, 1970, and Walsh, R., *Accts. Chem. Res.* 1981, 14, 246

⁶¹Zmbov, K. F.; Uy, O.; Margrave, J. L., *J. Am. Chem. Soc.* 1968, 90, 5090

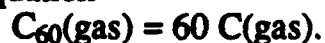
by Girifalco⁶² as 6.3 kJ/mol of carbon. Thus, the standard enthalpy change for the reaction

$\text{C}(\text{infinite graphite sheet}) = \text{C}(\text{g}), \Delta H^0_{\text{m}} = 710.4 \text{ kJ/mol}$,
can be taken as a measure of the covalent carbon-carbon bond energy in graphite. In atomizing a mole of infinite graphite sheets we break 3/2 moles of C-C bonds. Thus, the carbon-carbon bond strength in graphite is 474 kJ/mol.

We can estimate the resonance stabilization energy of the covalent bonding in graphite as follows. If resonance stabilization played no role, the bond energy in graphite would be 1/3 C=C bond energy + 2/3 C-C bond energy, or 444 kJ/mol. Since the actual bond strength is 474 kJ/mol, the stabilization energy in graphite is 30 kJ/mol of carbon. The accepted value for the resonance stabilization energy of benzene is $138 \pm 12 \text{ kJ/mol}$ of C_6H_6 , or 23 kJ/mol of carbon.

The carbon-carbon bond in C₆₀.

The atomization energy of carbon in fullerene, C_{60} , can be calculated from the equation



Using our value of 2193 kJ/mol for the heat of formation of $\text{C}_{60}(\text{solid})$, the heat of sublimation of C_{60} , and the heat of formation of $\text{C}(\text{gas})$ we calculate the total atomization energy of C_{60} to be 40769 kJ/mol C_{60} . There are 30 double bonds and 60 single bonds in most of the 12,500 Kekulé structures⁶³ of C_{60} , so the average energy of one C-C bond in C_{60} is $40769/90 = 453 \text{ kJ/mol}$. Again, if resonance stabilization were inoperative in C_{60} the average carbon-carbon bond strength would be 444.4 kJ/mol as it is in graphite, which also has a 2/1 ratio of single to double bonds. Thus, the resonance stabilization energy of C_{60} is 9 kJ/mol of bonds, or 810 kJ/mol of C_{60} .

VI. Gas phase absorption spectrum of C_{60} (manuscript in preparation)

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⁶²Girifalco, L., J. Chem. Phys. 1956, 25, 693

⁶³Brendsdal, E.; Cyvin, S. J., J. Mol. Struct. 1989, 188, 55-66

Introduction

Recent studies of Buckminsterfullerene, C_{60} , show that it sublimates at temperatures of above 400 °C. We decided to attempt a measurement of the gas phase absorption spectrum of C_{60} , in part to see if the material was stable enough at elevated temperatures to permit such a measurement, and in part to compare its gas phase electronic absorption spectrum with that of the solid and the solution phase.

Experimental Procedure

Approximately 1 mg samples of crystalline C_{60} purified by column chromatography as described above were placed into a 10 cm path length cylindrical quartz cell with suprasil windows, then baked in a high vacuum at 300 °C and sealed off. The cell was mounted at the center of a length of brass tubing which fitted inside a 25 cm long tube furnace. The cell windows were maintained at a temperature 7° to 10° higher than the center of the cell by means of two identical auxiliary heating coils built into the brass mounting, adjacent and just outside of the windows. Immediately beyond the heating coils were two additional suprasil windows. The whole assembly was symmetrical about the center with the lowest cell temperature at the center; this temperature was measured with a thermocouple in contact with the cell wall, and when constant is presumed to be the equilibrium temperature of the C_{60} in the cell. By using the auxiliary heating current as a fine adjustment, it was possible manually to hold the temperature to within ± 1 °C.

The radiation source was a deuterium lamp providing a continuum from 180 nm up to the visible range. By monitoring the observed intensity at the wavelength of the minimum absorption, it was possible to correct for slow drifts of the lamp intensity over observation times of hours. The transmitted radiation was measured in two ways:

(a) Using quartz lenses to collimate the radiation and focus it on the entrance slit of a McPherson grating monochromator from which the radiation was detected and recorded with a standard photomultiplier-picoammeter-computer combination. The lenses were not made of suprasil quartz, and so, below 200 nm, the intensity at the entrance slit was too small to give reliable absorbances.

(b) The same as (a), except that no lenses were used. The monochromator and, as much as possible, the spaces between the source, cell and monochromator slit were flushed with N_2 or Ar. The effectiveness of flushing was demonstrated by showing that the absorption of the Schumann-Runge absorption bands of O_2 could be reduced to a few percent

of their intensity in air and kept constant with time. Thus, reliable absorbances could be obtained between 180 and 220 nm. The resolution of the monochromator, as used, was estimated to be 0.2 nm by scanning the Hg emission lines at 313 nm.

Results

Figure 10 shows the ultraviolet absorbance of C_{60} gas at three temperatures: 500 °C, 550 °C, and 600 °C, taken with modification (a) above. These spectra are quite reproducible from day to day. After over a month of recording high temperature absorption spectra similar to these, the cell was opened and the contents dissolved readily in toluene, giving the characteristic C_{60} absorption spectrum. From this observation we conclude that, in the absence of oxygen, C_{60} retains its chemical identity for days even up to 600 °C.

Figure 11 shows one of the spectra recorded with the nitrogen-flushed optical path (modification (b)), which permits absorbance measurements down to 180 nm. The most notable feature of this spectrum, taken at 650 °C, is the relative intensities of the three peaks at 210, 258, and 332 nm. The 210 nm is almost 40% more intense than the peak at 258 nm; in contrast, the intensity of the 212 nm absorption peak of C_{60} in hexane is 30 percent less than that of the 258 nm peak.

In Figure 12 we show a plot of C_{60} vapor pressure versus temperature, computed from our data under the assumption that the molar absorptivities of C_{60} in the vapor are the same as in hexane solution. Also shown are recent determinations of the vapor pressure/temperature curve by Balooch et al⁶⁴ and by Mathews et al³². While the slope of the $\ln(P_{\text{vapor}})$ vs $1/T$ plot give a heat of sublimation of 159 ± 12 kJ/mole from our data, in good agreement with the data of Mathews et al, the assumption of equivalent molar absorptivities of C_{60} in gas and in solution must be in error, since our vapor pressure curve is a factor of 1.5-3 higher than that of the other two measurements.

We are investigating further these subtle differences between the gas phase and solution phase spectra of C_{60} , and are in the process of making a detailed comparison of gas phase and solution phase molar absorptivities for C_{60} .

⁶⁴Abrefah, J.; Olander, D. R.; Balooch, M.; Siekhaus, W. J., *Appl. Phys. Lett.* 1992, 60, 1313

VII. Some thoughts on the implications of these results for CRDEC.

The fullerenes may well provide a new route to interesting and novel new adsorbent materials. The fact that fullerenes are far more reactive than originally thought is borne out by the difficulty we are having in obtaining pure samples, as well as the ease with which C_{60} is functionalized. For example, L. Chiang⁶⁵ at Exxon has succeeded in functionalizing fullerenes with hydroxyl groups, producing a compound of formula $C_{60}(OH)_{24}$. This material becomes extremely hydroscopic! The hydroxyls can also function as sites for further chemical modification of fullerenes, e.g., by esterification. Exxon has taken out four patents on these fullerol materials. Fred Wudl and colleagues have functionalized fullerenes with amines. Amos Smith and colleagues at Penn have made $C_{60}O$ and, more recently, $C_{60}(CH_2)$, in which the methylene bridges the bond between two six-membered rings. In other words, the substitutional chemistry of fullerenes is steadily becoming understood.

It is certainly in CRDEC's interest to retain an active research program in fullerene chemistry so that the surface of fullerenes can be functionally modified to enhance absorbent properties. As CRDEC assesses the importance of fullerenes as novel adsorbents, it will be important to provide highly pure and well characterized samples for further experimental studies. If any fullerenes are ever incorporated into air purification devices, it will be useful to know that polynuclear aromatic hydrocarbons, which are potential carcinogens, have been eliminated from the absorbent materials.

VIII. Note on personnel

In experimental work of the type that we are doing, continuity of personnel is very important. One of the key members of my experimental group has been Professor Li Dayin, a Visiting Scholar at Drexel University who has a faculty appointment in physical chemistry at Beijing Normal College. Professor Li has done the outstanding solubility measurements discussed above while being supported under the auspices of the Chinese government during the period of this contract.

⁶⁵Chiang, L.; Swirczewski, J. W.; Hsu, C. S.; Chowdhury, S. K.; Cameron, S.; Creegan, K., J. Chem. Soc. Chem. Comm. , , 1993, in press

Table 1. Correlation of FTIR and percent hydrogen content of C60 samples.**% H determined by Rutherford backscattering and neutron activation analysis.****intensity ratio determined from FT-IR**

C60 sample identification	date of FTIR spectrum	composition information	atom fraction H *	FT-IR intensity ratio**
NIST (1991)	9/3/92	".0057H/C"	0.0057	3.2
bad C60, Kniaz	8/13/92	"C60, H6"	0.1	19.4
C60, H 0.3 Kniaz	9/17/92	"C60, H 0.3"	0.005	2.7
Penn 200	10/13/92		0 #	1.7
Penn 220 residue	11/23/92		0 #	1.7
C60, H1.0 Kniaz	9/17/92	"C60, H1.0"	0.017	2.2
Penn 220 sublimate	11/23/92		0.001 @	1.8
Penn 202	10/13/92		0.012 @	4
Extriumf/MC-1-66A	9/3/92		0.065 @	13.2

* atom fraction = (atoms of H)/(atoms of H + atoms of C)

**ratio = [int.(2760 - 3100 cm⁻¹)/int(2620-2760 cm⁻¹)]

atom fraction H defined to be zero in these samples

@ computed atom fraction H from linear regression fit to first five points

Table 2. Summary of Experimental Calorimetry Results: Heat of Combustion of C₆₀

Calibration Results	Experimental Results
2518.803 J·K ⁻¹	-35806.22 J·g ⁻¹
2518.095	-35810.67
2517.727	-35798.46
2518.218	
2517.562	
2517.881	
<hr/>	
$\overline{2518.05 \pm 0.18 \text{ J·K}^{-1}}$	$\overline{-35805.1 \pm 3.5 \text{ J·g}^{-1}}$
<hr/>	

Table 3. Summary of the Thermochemical Results for C₆₀

$\Delta_c U_m^0(\text{C}_{60}, \text{cr}, 298.15 \text{ K}) = -(25803.9 \pm 5.6) \text{ kJ·mol}^{-1}$
$\Delta_c H_m^0(\text{C}_{60}, \text{cr}, 298.15 \text{ K}) = -(25803.9 \pm 5.6) \text{ kJ·mol}^{-1}$
$\Delta_f H_m^0(\text{C}_{60}, \text{cr}, 298.15 \text{ K}) = (2193.3 \pm 9.6) \text{ kJ·mol}^{-1}$

Table 4. Experimental Determinations of the Enthalpy of Formation of Solid C₆₀

Beckhaus et al	Steele et al	Our results
2280 ± 12 kJ/mole	2422 ± 12 kJ/mole	2193 ± 10 kJ/mole

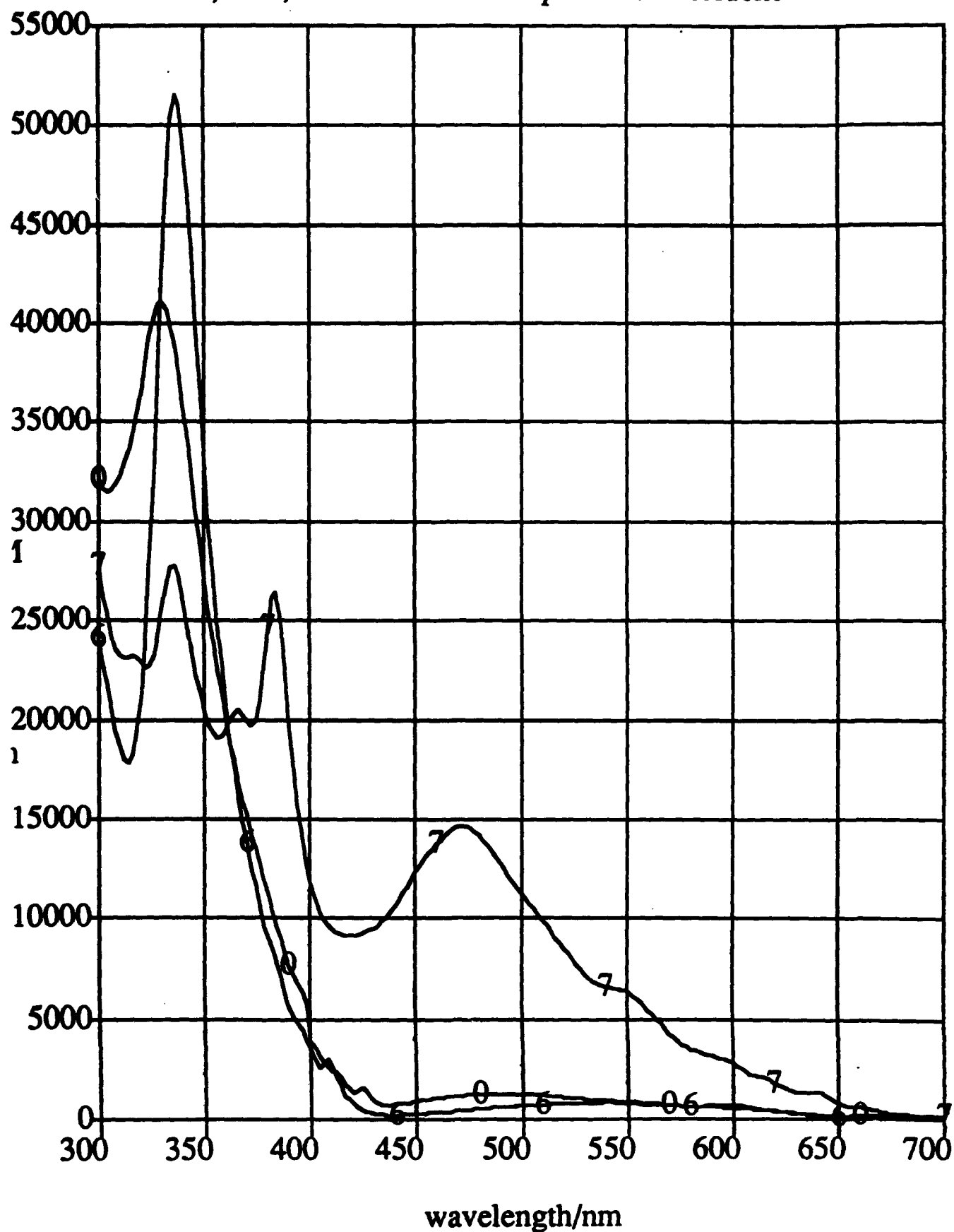


Figure 1A. Molar Absorptivity of C₆₀, C₇₀, and C₆₀O in Toluene; 300 - 700 nm

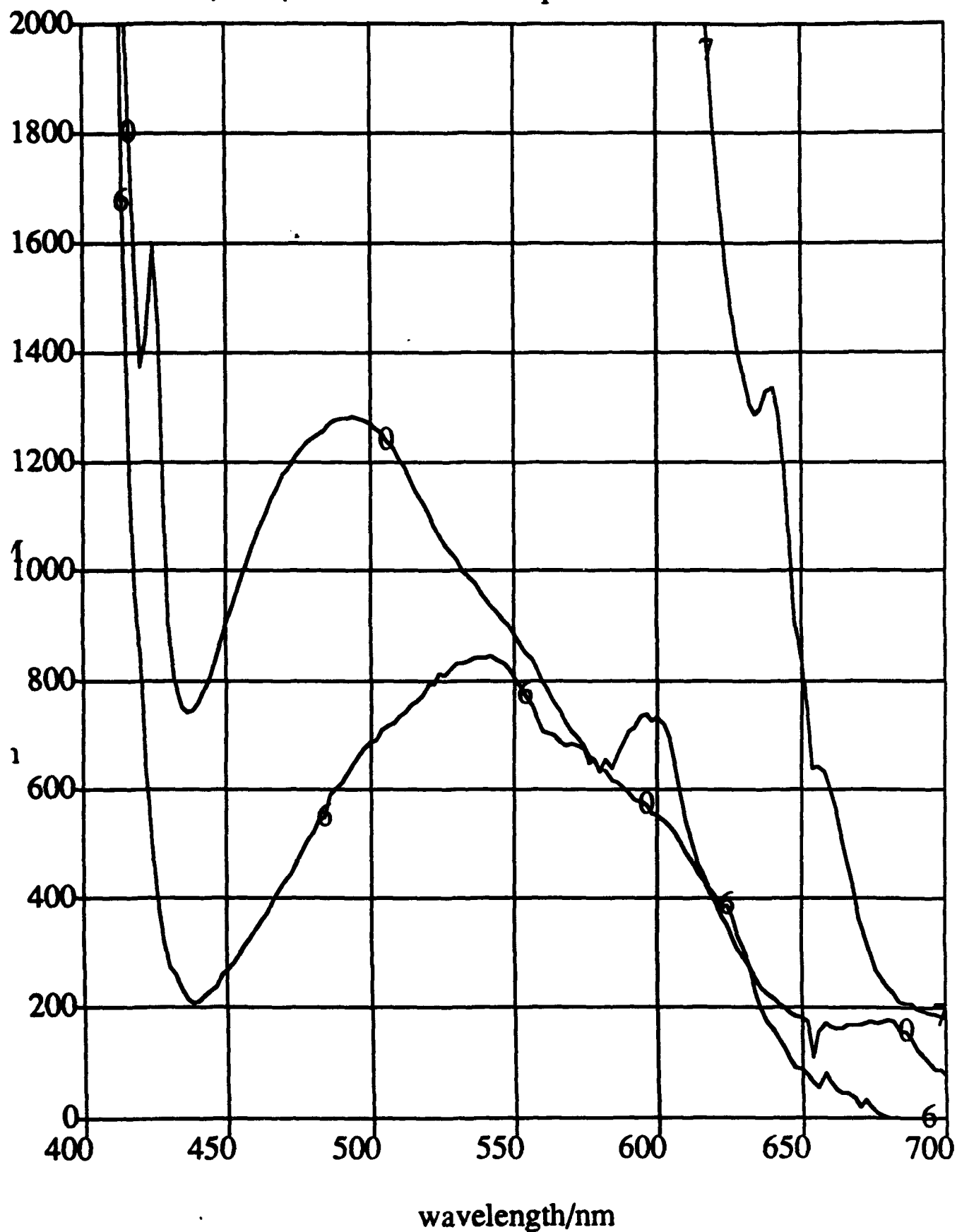


Figure 1B. Molar Absorptivity of C₆₀, C₇₀, and C₆₀O in Toluene; 400 - 700 nm

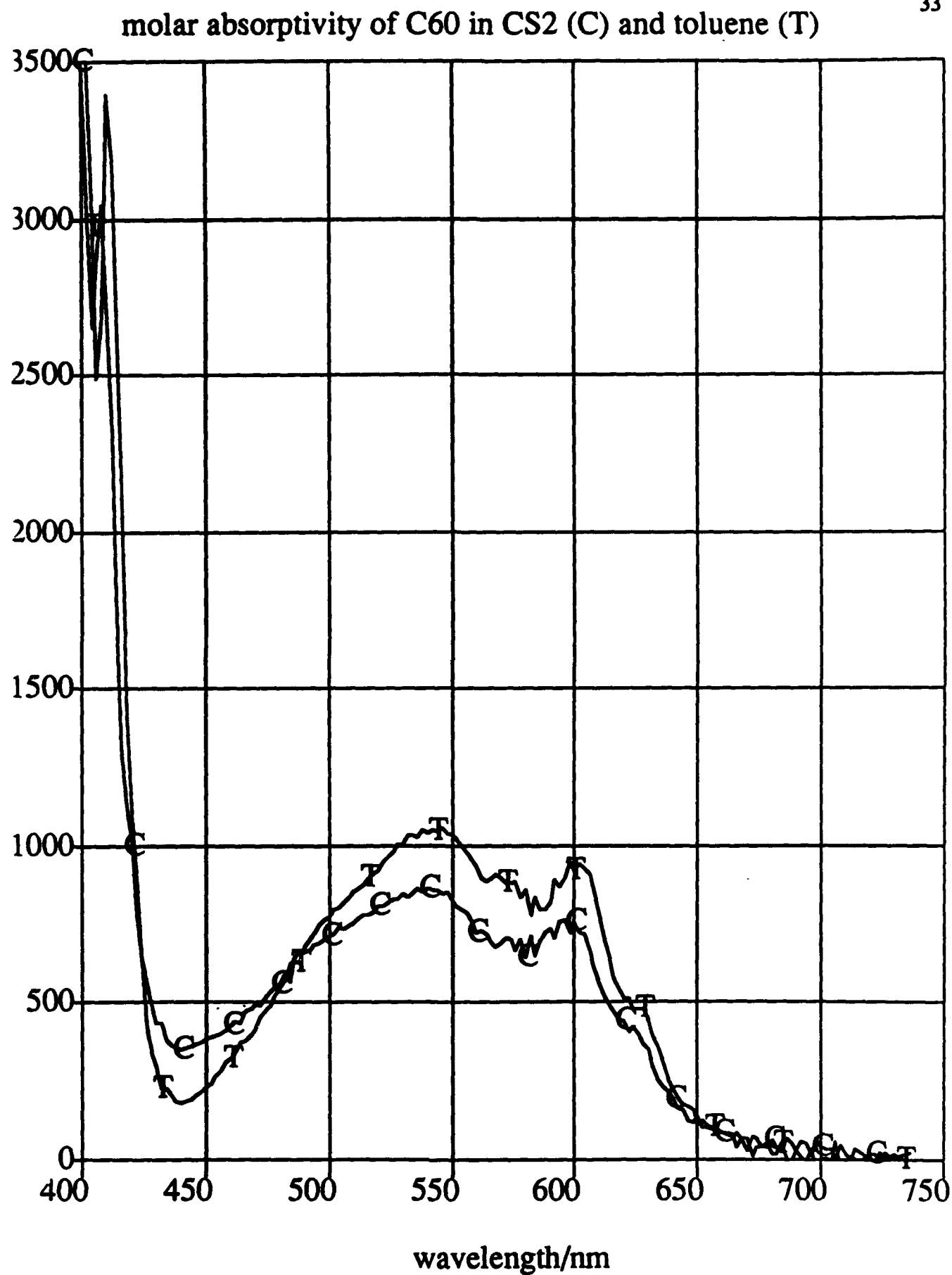


Figure 2. Molar Absorptivity of C₆₀ in CS₂ and in Toluene: A Comparison

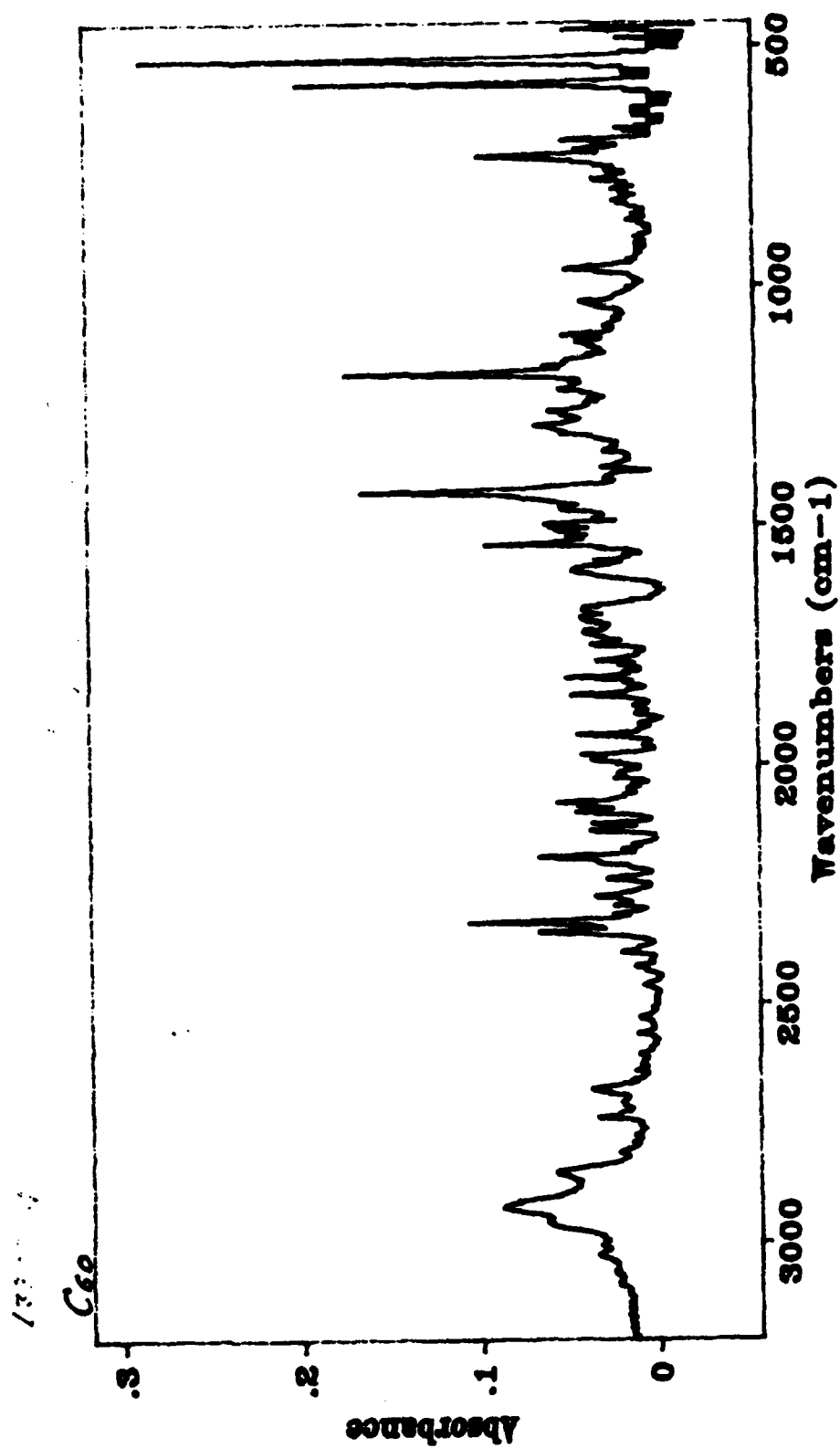


Figure 3A. Diffuse Reflectance FTIR Spectrum of C_{60} Sample with Residual Hydrocarbon; (Note C-H Stretch Band Region, 2800 - 3050 cm^{-1})

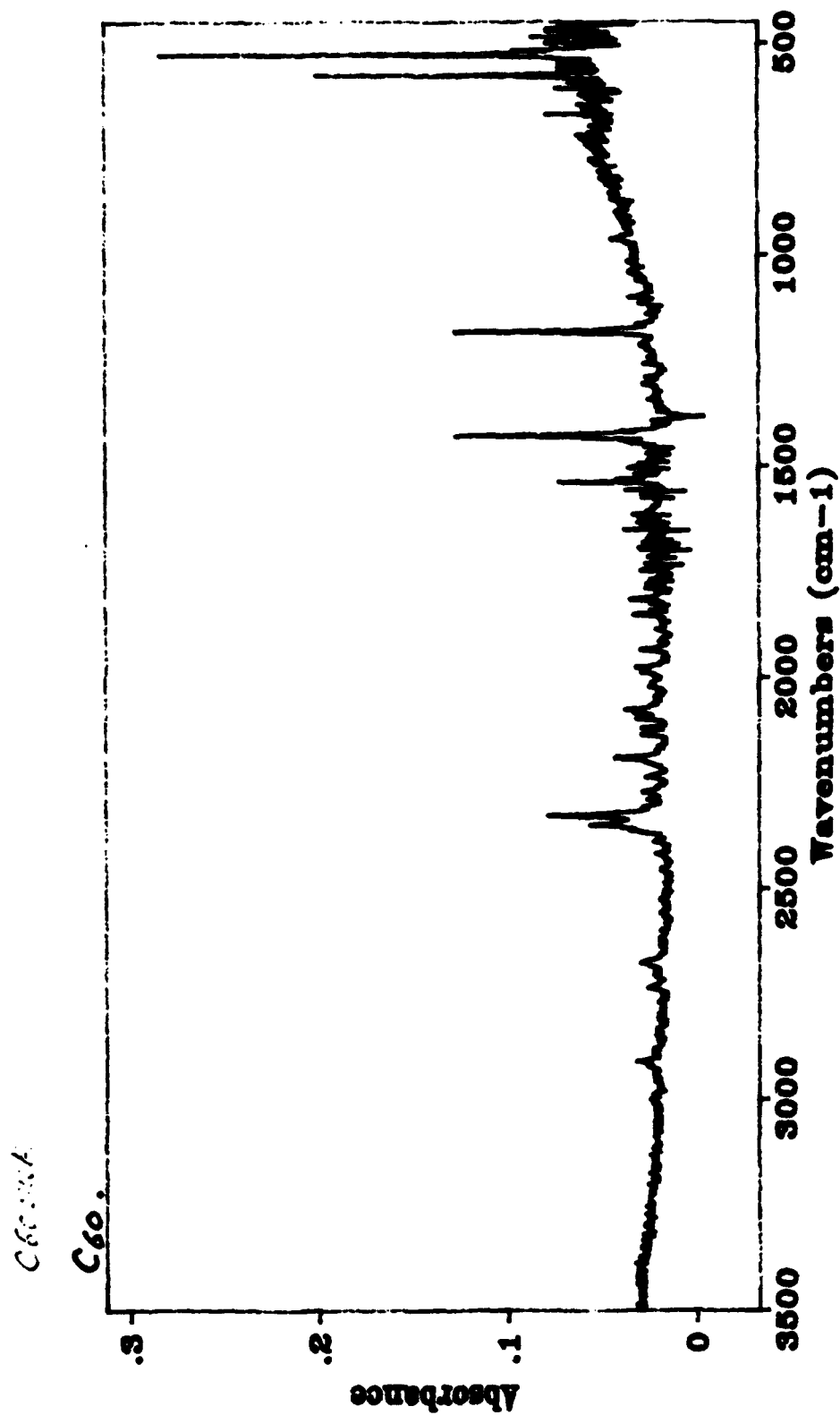


Figure 3B. Diffuse Reflectance FTIR Spectrum of Sublimed C₆₀ Sample; (Note the Absence of C-H Stretch Bands)

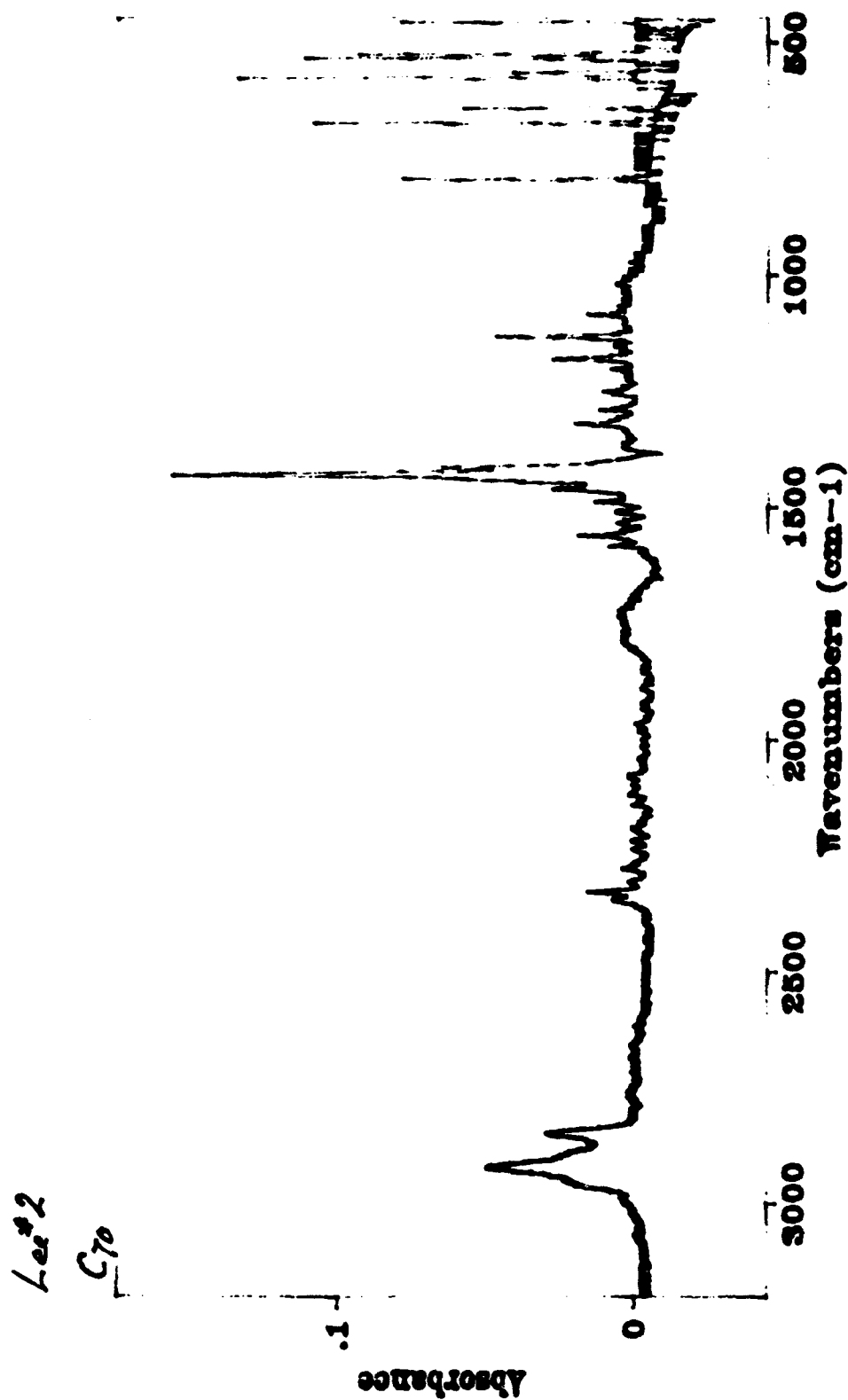


Figure 4A. Diffuse Reflectance FTIR Spectrum of C₇₀ Sample with Residual Hydrocarbons

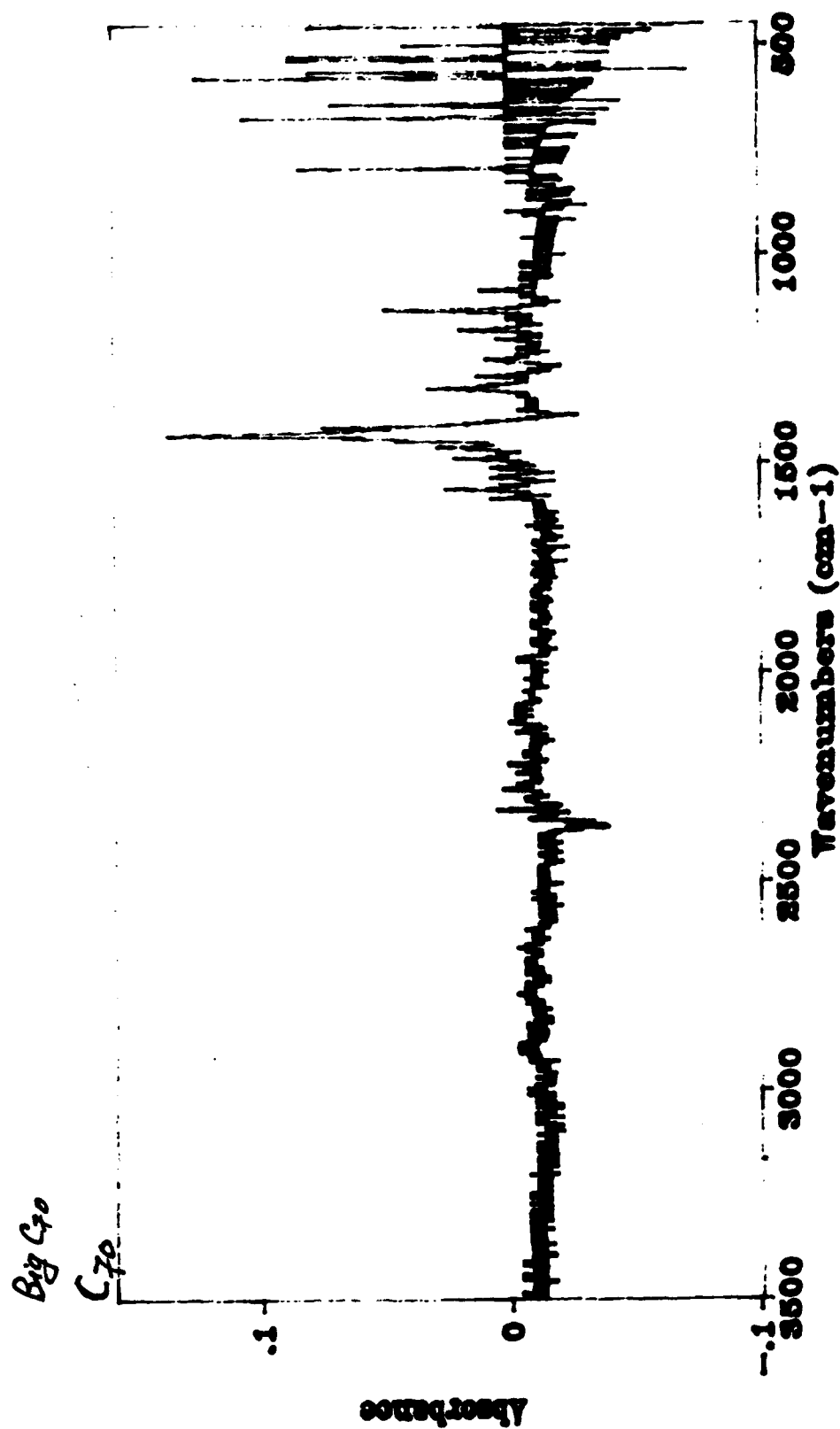


Figure 4B. Diffuse Reflectance FTIR Spectrum of Sublimed C₇₀

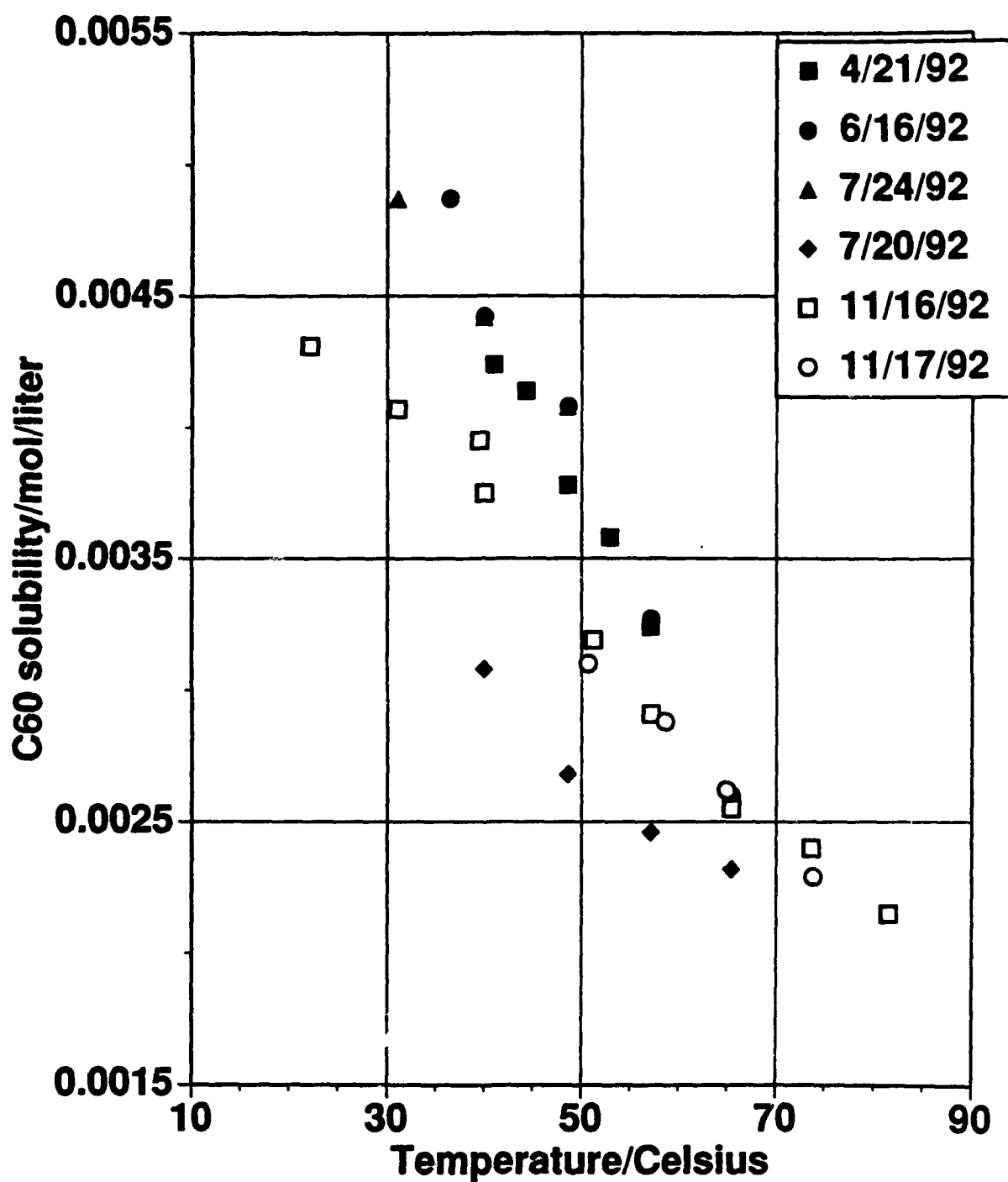
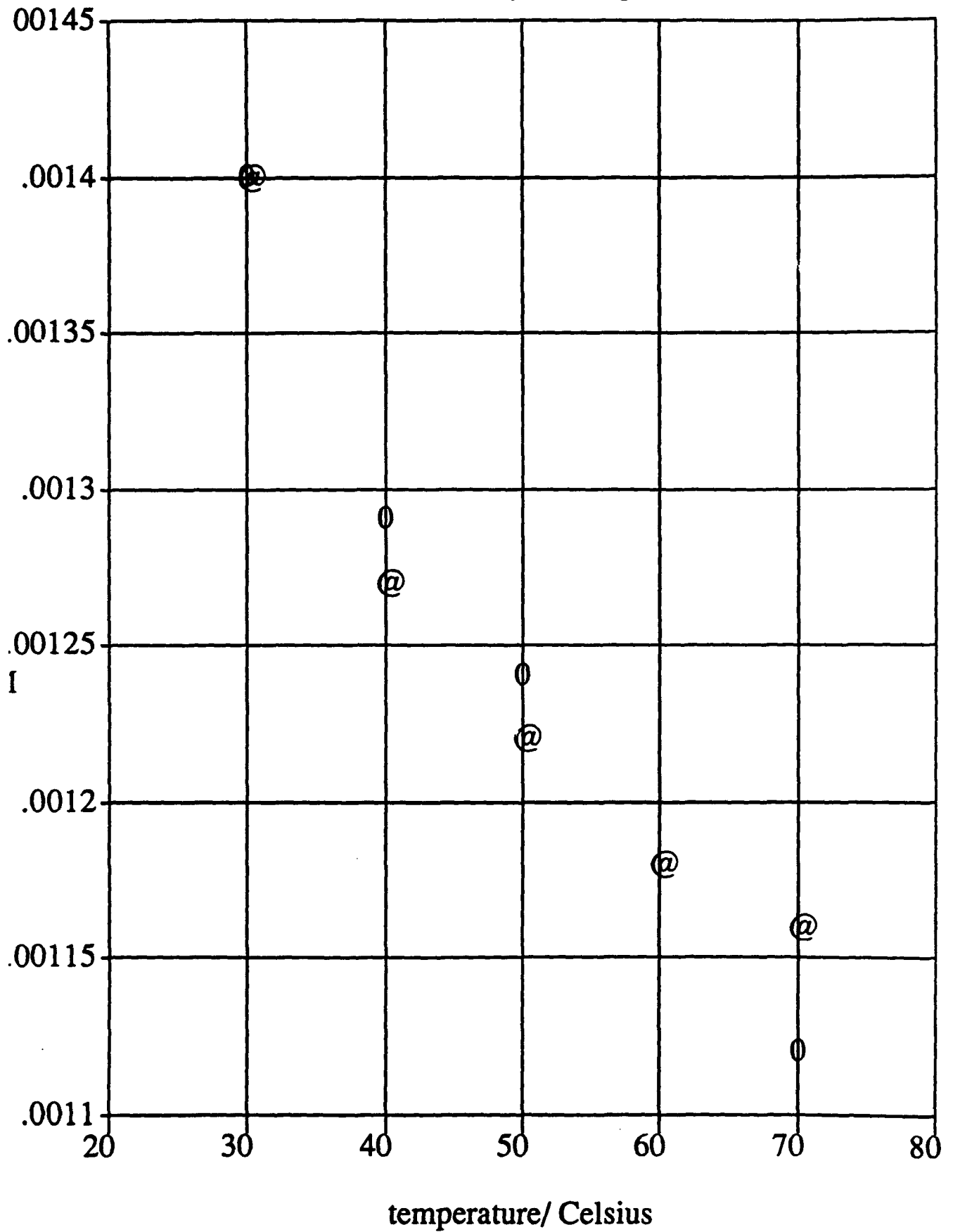
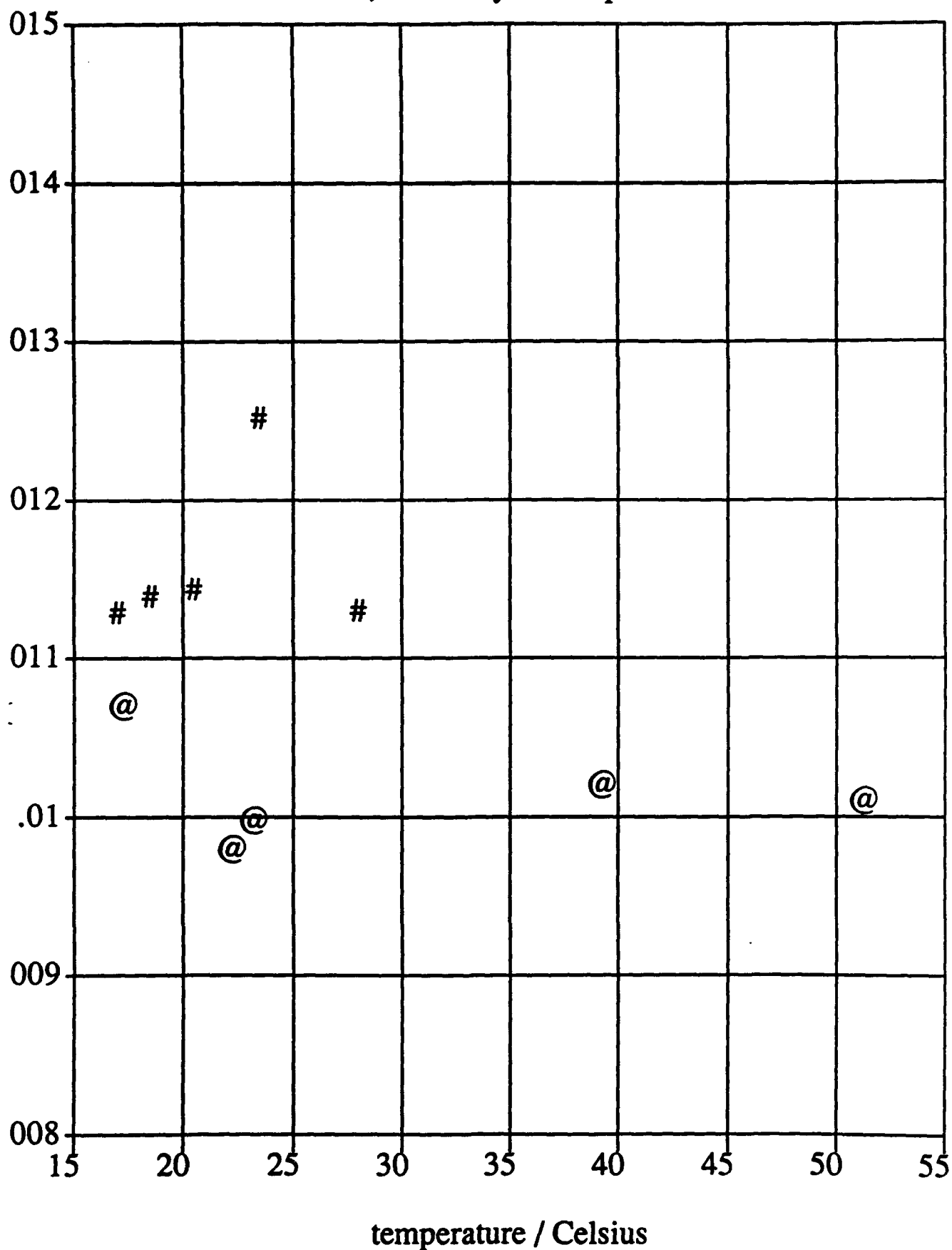


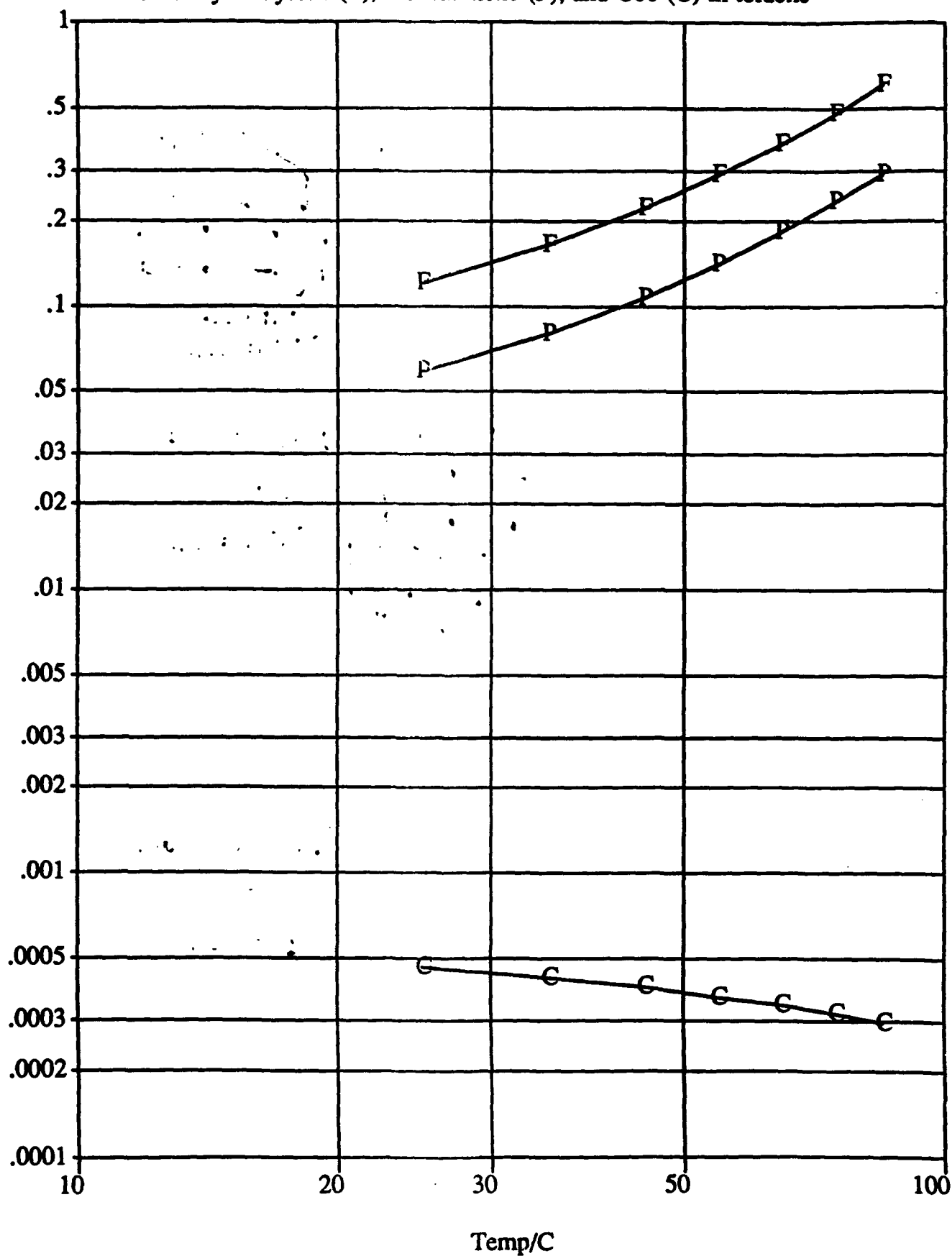
Figure 5. The Solubility of C₆₀ in Toluene as a Function of Temperature

C70 in toluene, solubility vs temperature

Figure 6. The Solubility of C₇₀ in Toluene as a Function of Temperature

C60 in CS₂, solubility vs temperatureFigure 7. The Solubility of C₆₀ in Carbon Disulfide as a Function of Temperature

Solubility of Pyrene (P), Fluoranthene (F), and C60 (C) in toluene

Figure 8. Temperature Dependence of the Solubility of Fluoranthene, Pyrene, and C₆₀

Enthalpy of Formation of Different Allotropic Forms of Carbon (kJ per mole of C)

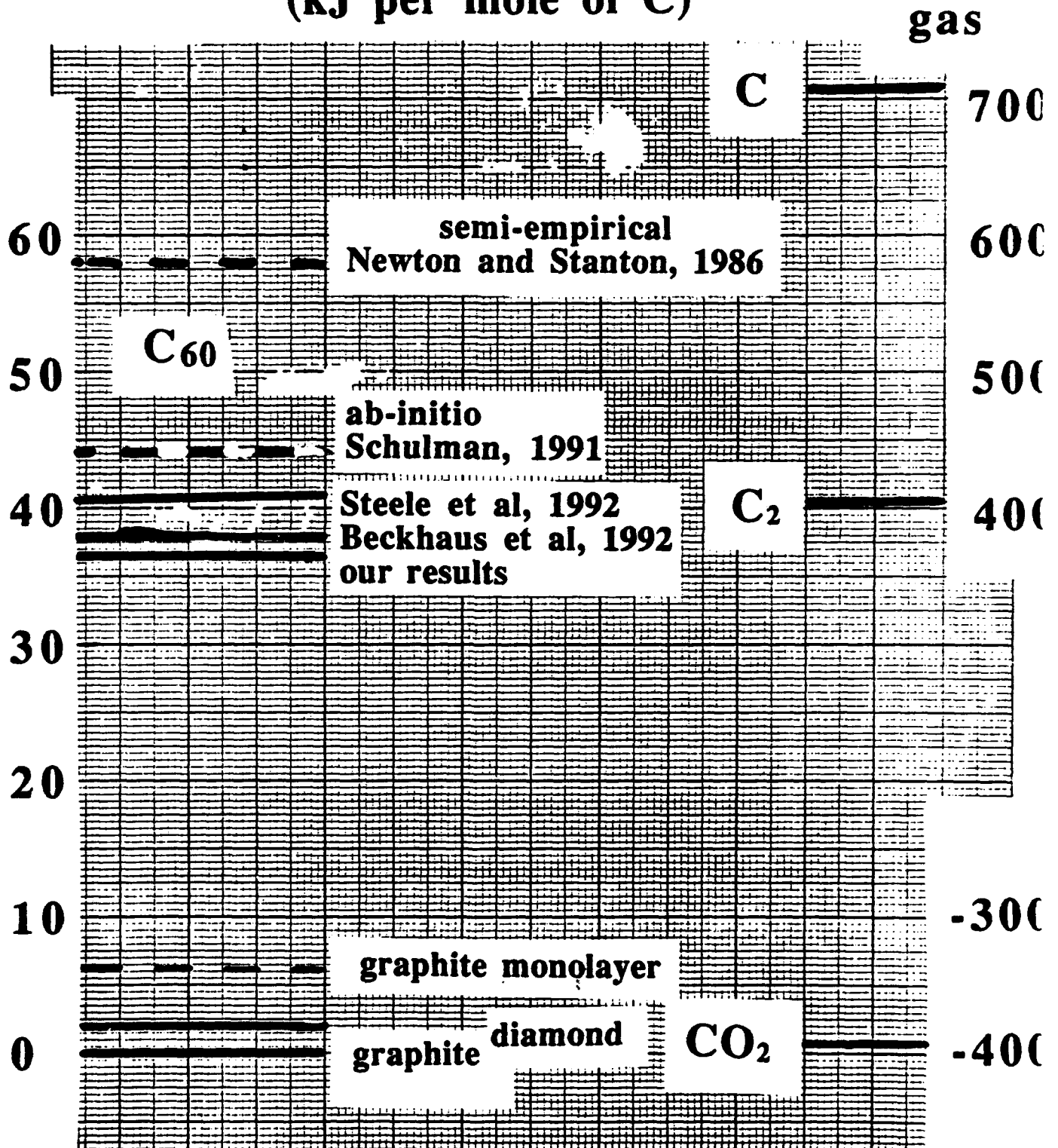


Figure 9. Enthalpy of Formation of Different Allotropic Forms of Carbon

averaged C₆₀ gaseous absorbances, 1/7/92: 500C [1]; 550C [2]; 600C [3]

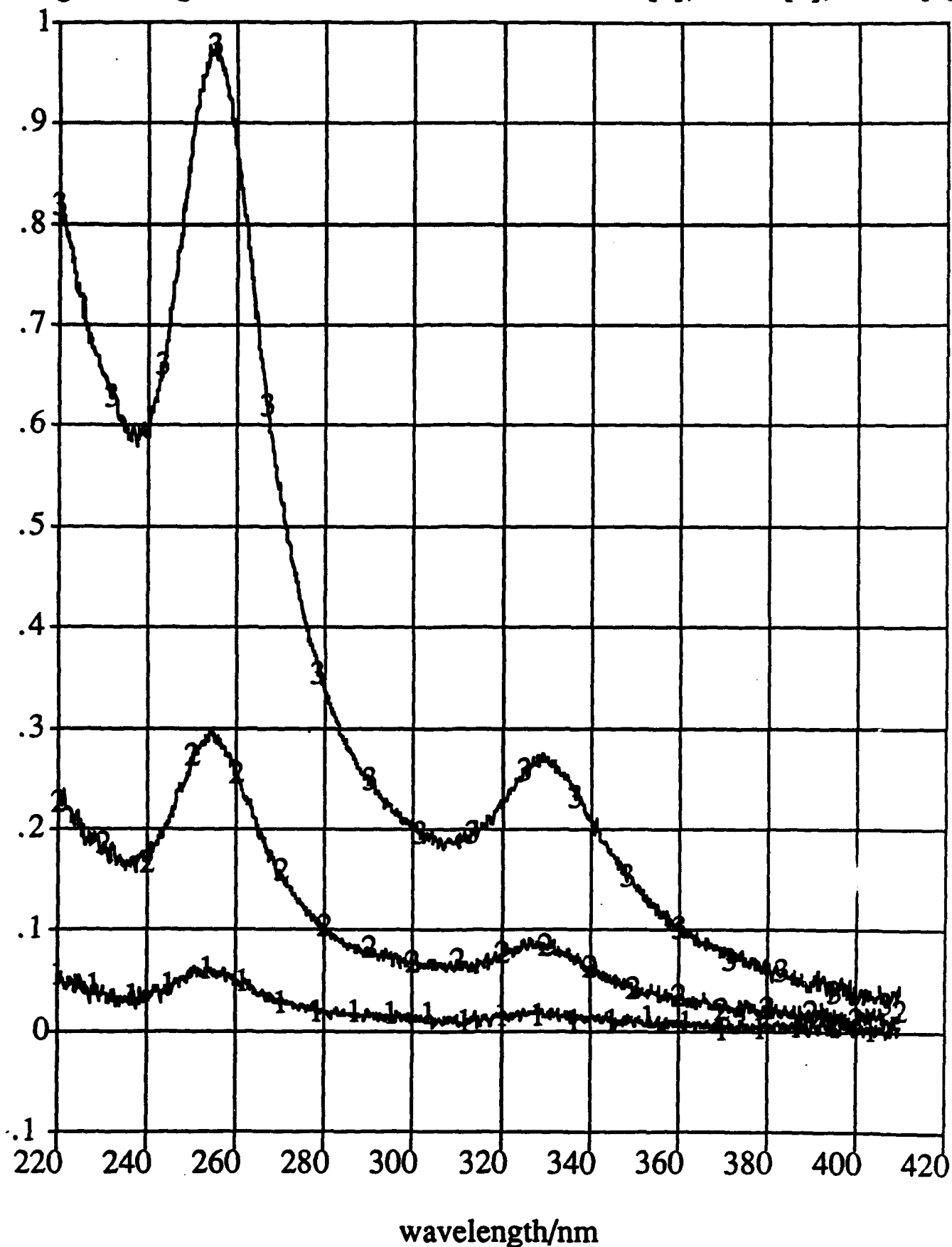
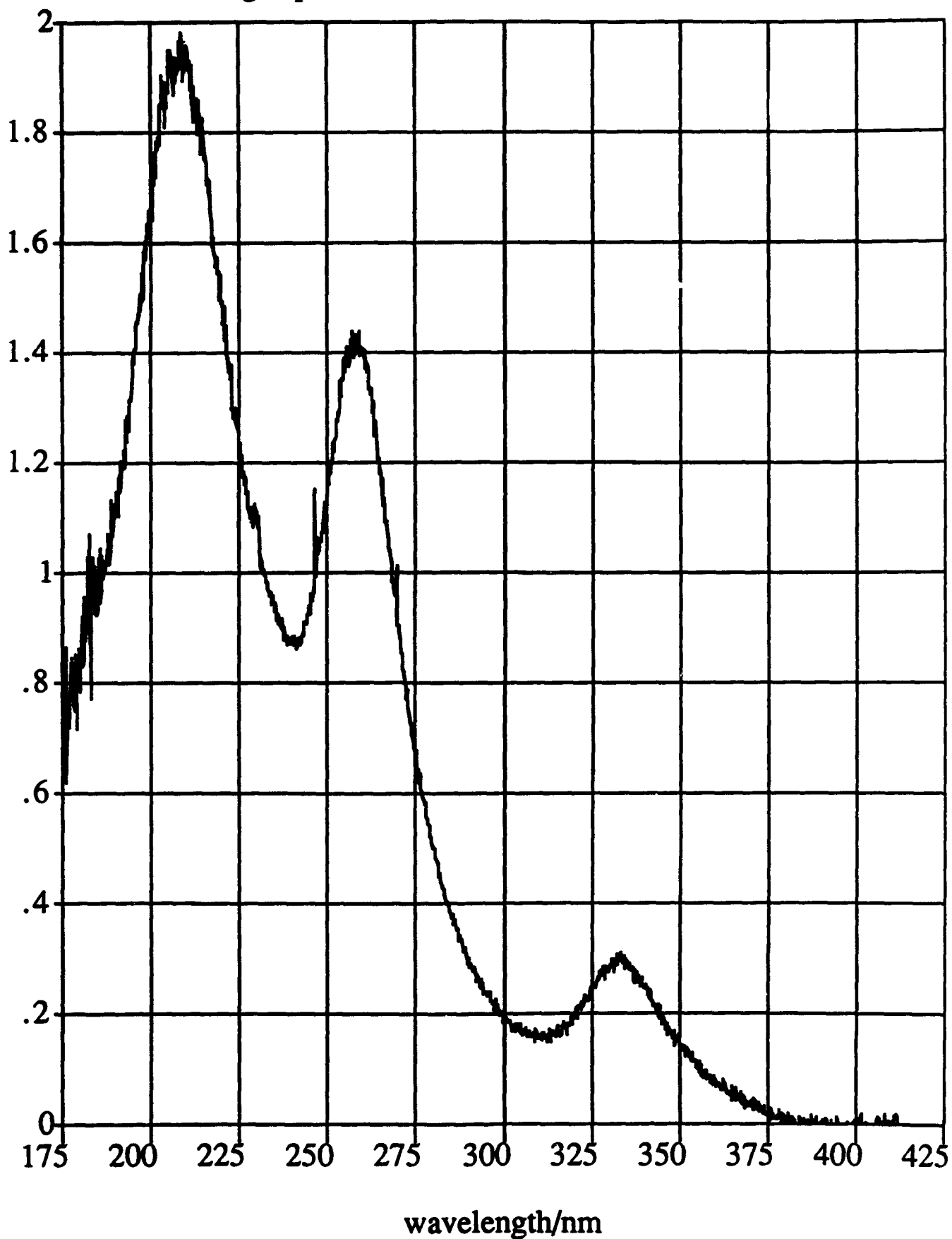


Figure 10. Ultraviolet Absorbance of C₆₀ Gas at 500 °C, 550 °C, and 600 °C, 220 < λ < 400 nm, Cell Pathlength = 10 cm

C60 gas phase absorbance at 650 C, 1/10/92

Figure 11. Ultraviolet Absorbance of C₆₀ Gas at 650 °C, 180 < λ < 400 nm

C60 vapor pressure:*, this work; B, Balooch; M, Mathews

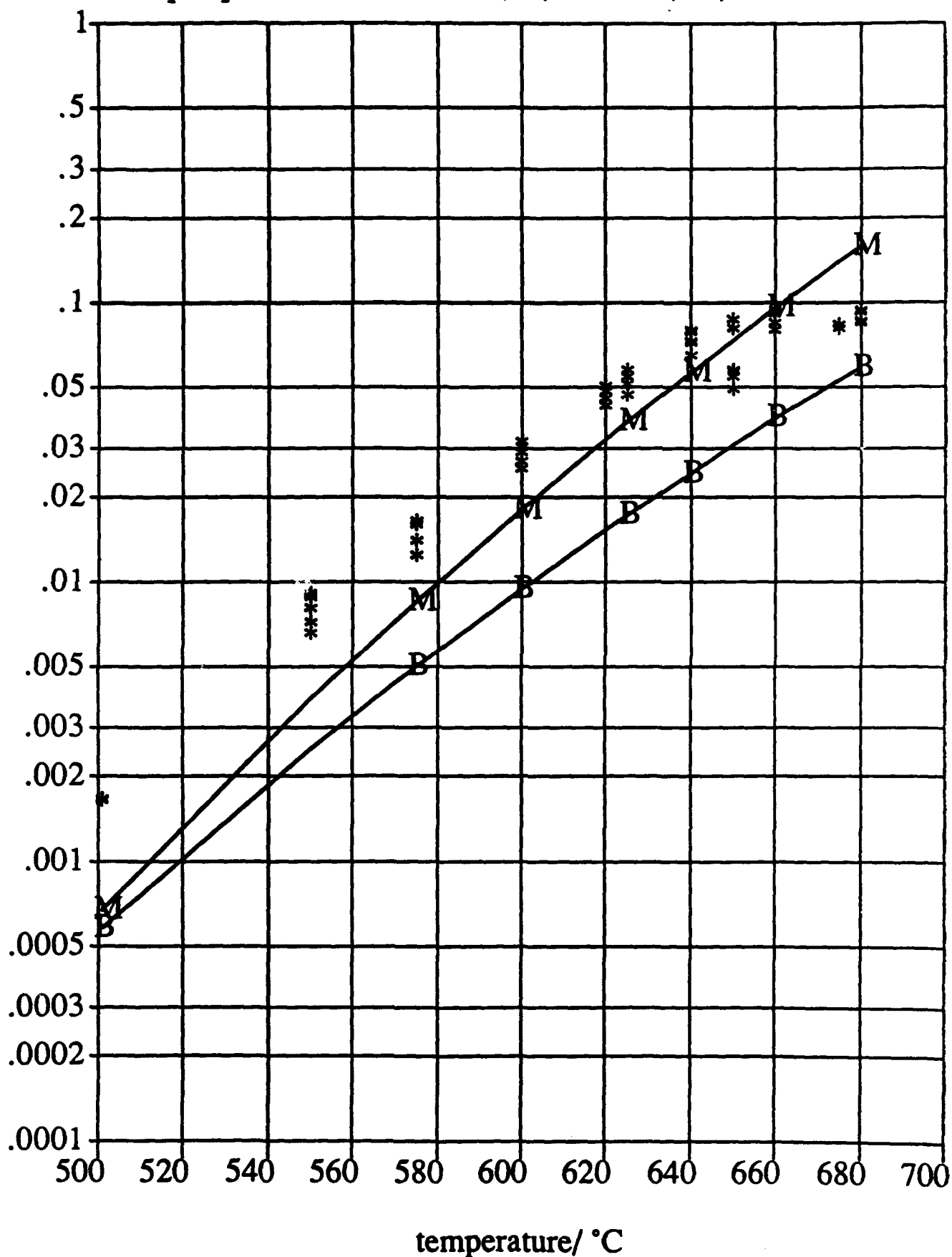


Figure 12. Vapor Pressure of C₆₀ as a Function of Temperature